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Synthesis and Characterisation of Semiconducting Polymers for OLEDs Application

A Major Project Dissertation Submitted to the Faculty of Technology,

University of Delhi

Towards the Partial Fulfilment of the Requirements for
Award of the Degree of

Master of Engineering
in
Polymer Technology

Submitted by

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Certificate

This is to certify that Mr Rajesh Kumar Jha a student of Final Year of Master of Engineering. (Polymer Technology). College Roll No 05/Poly/02. from Delhi College of Engineering, (University of Delhi). Delhi-110042 has individually completed a dissertation entitled **"Synthesis and Characterisation of Semiconducting Polymers for OLEDs application"** is a bonafied record of his work carried out under our joint supervision in the Division of Engineering Materials OLEDs Lab (Polymeric and Soft Materials Section) at National Physical Laboratory K S Krishnan Road New Delhi-110012

Further it is also certified that this dissertation has not been submitted for any other degree or diploma in any other college or university to the best of our knowledge

He bears a good moral character and we wish him all success in his life

The project work has been carried out from 15th December 2003 to 31st May 2004 at National Physical laboratory, New Delhi-110012.

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Rajesh Kumar Jha

Dedicated to my childhood tutor
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Abstract

Organic Light Emitting Diodes (OLEDs) are a new type of thin emissive display devices predicted to possess superior properties to existing display technology e g Liquid Crystal Display (LCD). The main advantages of these devices are low power consumption and a thin flexible display structure The report on "**Synthesis and Characterisation of Semiconducting Polymers for OLEDs Application**" contains a description of the emissive device structures, the physics of the organic layer structures in an OLED and routes to synthesise polymers and oligomers The experimental section consists of the synthesis of three materials poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylenevinylene] (MEH-PPV), poly(p-phenylenevinylene) (PPV) and p-sexiphenyl and fabrication of light emitting diodes applying these materials as light emitting layer The main purpose of device fabrication was to analyse the application of these materials as electroluminescent material The electroluminescence (EL) spectra and Current Voltage (I-V) characteristics of these devices were recorded and analysed to understand the characteristics of materials and their application as electroluminescent layer in organic light emitting diodes Materials were characterised by UV-Vis absorption spectra, Photoluminescence (PL) spectra, Fourier Transform IR spectra and Thermo-gravimetric Analysis (TGA) Though the evaluation of the OLED revealed the main disadvantage of an unsatisfactory lifetime, the results of device characteristics, particularly ITO/PPV/CdS/Al double layered diode, is found highly promising

Introduction

Since last decade or so, there has been significant interest in electroluminescence from organic materials, particularly polymers Driven by the potential to significantly impact the information display market, research and development in organic light emitting devices have advanced at a remarkable pace The organic light emitting devices have many futuristic applications, which could be realised sooner or later are large screen on walls for TV and video observation with wide viewing angle, large electronic bill boards, low glare illumination with two dimensional lighting system, light emitting wallpaper and active clothing etc all at a low cost

Efficient electroluminescence (EL) from organic material was first reported in 1987 by a team of researchers at Kodak Previous work on organic electroluminescence (EL) using thick single crystals was deemed impractical due to high voltage and low EL efficiencies However, the Kodak report demonstrated that thermally evaporated, amorphous thin films of small molecules could be utilized to produce an efficient, low voltage OLED Few years later Friend and co-workers at Cambridge University demonstrated efficient electroluminescence(EL) from a spin coated organic polymer Unlike small molecules, which are vacuum deposited, polymers are solution processed and may potentially offer an inexpensive route to the manufacture of large area display

An organic light-emitting device consists of one or more semiconducting organic thin films sandwiched between two electrodes -one of which must be transparent Usually indium tin oxide (ITO) is utilised as the transparent anode and evaporated metal is utilised as the cathode The device is fabricated by sequentially depositing the organic

thin films followed by a shadow mask defined thin metal cathode onto a transparent substrate such as glass or a flexible plastic When a forward bias is applied, injected electrons and holes recombine in the organic layer to generate light

While most early molecule and polymer devices were relatively inefficient and short lived, enormous progress has been made in both the efficiency and lifetime of these devices over the past decade. Much work still remains to understand the intrinsic mechanisms of degradation and to increase lifetime for higher brightness applications

In the present report, three organic materials like poly(p-phenylenevinylene) (PPV), poly[2-methoxy-5-(2'-ethylhexyloxy)-p- phenylenevinylene] (MEH-PPV) and p-sexiphenyl were synthesised and characterised by taking different optical and thermal methods like UV-Vis spectra, Photoluminescence (PL) spectra, Fourier Transform IR spectra and Thermo-gravimetric Analysis (TGA). The synthesised materials were directly used for device fabrications The fabricated devices of the following configurations- ITO/PPV CdS/Al, ITO/MEH-PPV/Al and ITO/p-sexiphenyl/PBD/Al were studied The devices so fabricated were characterised by their Electroluminescence (EL) spectra and Current-Voltage (I-V) Characteristics On applying a bias voltage (more than 15V) to the device with configuration ITO/MEH-PPV/Al produced a week orange-red electroluminescence (EL) and the lifetime of the device was found very short While in case of device structures ITO/p-sexiphenyl/PBD/Al and ITO/PPV/CdS/Al needed a bias voltage in the range of 5-6V and blue and yellow-green electroluminescene (EL) were observed respectively which was visible in normal light and lifetime of the devices were found better than the first device.

OLEDs: An Introduction

1.1. Historical Evolution

Human has been using the materials available in nature since prehistoric time for betterment of human life and evolution of intelligent society. As human intelligence evolved his needs increased day by day. A pursuit for better and still better materials drove his passion and we see the sea change in the field of scientific invention. Fire was one of the simplest ways for prehistoric human to illuminate his dwellings. Since then a great change has been seen the way we have been illuminating our dwellings. Safe illumination, which always was a great challenge for human being, seems to come its end in near future. Electroluminescence is one of the scientific discoveries in the last century that changed the life of mankind immensely. Now the electroluminescence from polymeric materials will certainly change not only the way we illuminate our home but also our life style.

In contrast to photoluminescence (PL), the light emission from an active material as a consequence of optical absorption and relaxation by radiative decay of an excited state, electroluminescence (EL) is a non-thermal generation of light resulting from the application of an electric field to a substrate[1,2]. In the latter case, excitation is accomplished by recombination of charge carriers of opposite sign (electron and hole) injected into an inorganic or organic semiconductor in the presence of an external electric field[3,4].

This phenomenon was first discovered for inorganic materials in 1936, when Destriau et al. observed high field electroluminescence from a ZnS phosphor powder dispersed in an isolator and sandwiched between two electrodes[3,5]. General Electric

introduced first LED based on inorganic emitter GaAsP in market in early 1960s Later it was found that the materials that were generally used for inorganic LEDs are compounds of elements from group 13, 14 and 15 of the periodic table such as GaAs, GaP, AlGaAs, InGaP, GaAsP, GaAsInP and more recently AlInGaP Semiconductors with large band gaps are difficult to obtain so the blue LEDs Nevertheless, blue inorganic LEDs based on SiC, ZnSe, or GaN were developed, but exhibited distinctly lower efficiencies in comparison to others[3-6] Since last few decades a lot of development is seen in the field of inorganic LEDs. Light emitting diodes (LEDs) of various colours with good quantum efficiencies have been fabricated and its economic benefit was exploited worldwide.

Destriau's discovery of electroluminescence (EL) in inorganic compounds (ZnS, phosphors) in 1936 and the discovery in 1947 that a transparent anode could be constructed by depositing a layer of Indium Tin Oxide (ITO) onto a glass surface opened the possibility of obtaining light emitting planar surfaces[7]

The fact that many aromatic organic molecules are photoluminescent suggested their use as electroluminescent materials In 1963, Pope et al reported electroluminescence (EL) from an organic semiconductor They observed emission from single crystals of anthracene, a few tens of micrometers in thickness, using silver paste electrodes and required large voltages to get emission typically 400V[8] Helfrich and Schneider made similar studies in 1965 using liquid electrodes Considerable effort has been taken to understand the basic mechanism as well as to provide stable electroluminescent devices Development of organic thin film electroluminescence (EL) advanced with the study of thin film devices. In 1982, Vincett et al. reported blue

electroluminescence (EL) from anthracene sublimed onto oxidised aluminium as one electrode, and were able to reduce voltage considerably, for example, to 12 V [7,8]

In 1983, the discovery of electroluminescence (EL) in poly(vinylcarbazole) led to a search for other electroluminescent materials covering other ranges of the visual spectrum. However, the development of electroluminescent organic devices was not successful at that point due to the relatively poor lifetime and relatively low efficiency. Organic electroluminescent devices proved not to be competitive with incandescent light sources, and essentially all research was focused on traditional inorganic electroluminescent materials, since light emitting devices (LEDs) based on these materials have been commercially available since 1960s [7,9]

In 1987, the group of Tang and Van Slyke at Eastman-Kodak demonstrated efficient electroluminescence (EL) in two layer sublimed molecular film devices comprised of a hole transporting layer of an aromatic diamine and emissive layer of 8-hydroxyquinoline aluminium (Alq3) [9,13] This result provided a basic design for light emitting diode architecture, which was applicable to systems employing low molecular weight electroluminescent materials. The technique they used to emit light was to vacuum deposit small molecules to form a layered structure The layered device structure was produced on an ITO (anode acts as hole injection layer) coated glass substrate over that electroluminescent material and a magnesium-silver alloy (cathode acts as electron injection layer) were vacuum evaporated one by one The thin film layered structure permits a high electrical field at low voltage. Thus, light from thin film organic materials is usually produced at low voltage. High quality thin molecular layers were an important condition for the development of OLEDs [7,8].

In 1990, Burroughes et al. at the Cavendish Laboratories at Cambridge University presented the first LED using polymers as active material[14]. The active material used was a conjugated polymer[3,13]. In comparison to the traditional solid state LEDs, the new organic approaches were believed to be much more efficient. In nature, organic materials are in some cases able to perform in a chemical way a 100% relationship of energy consumption versus emission of light, e.g. the fireflies. Unfortunately such high efficiency is unrealistic in fabricated electroluminescent devices[7,9,12].

Conjugated polymers, and small molecules (oligomers and metal complexes/chelates) are considered as the two classes for OLEDs[7]. Despite of the fact that the two approaches only emitted a small amount of light that lasted only a few minutes, it caused a major interest among other researchers and companies. Much because of the predicted features of the organic displays would overcome the advantages for other display techniques, e.g. low voltage, low weight and wide viewing angle.

The above classifications of light emitting organic layers in the organic light emitting devices both possess luminescent and conductive properties. To achieve accurate functions of the material, a modification of the specific characteristics of the material are often done. Oligomers and small molecules have molecular structures of relatively short characteristics and consequently low molecular weights. The most commonly used material with the most explored properties among the small molecules are hydroxyquinoline aluminium (Alq3) and oligomer p-sexiphenyl.

Conjugated polymers are composed of a long repeating chain of similar smaller molecules, called monomers. They possess consequently, compared to small molecules, a

molecular weight twenty to fifty times higher A frequently used conjugated polymer is the poly(p-phenylenevinylene) (PPV)

1.2. Electroluminescence in Organic Materials

Since in general polymers and organic materials are not referred as conducting materials because of their large band gap, a very high electrical field has to be applied to conduct electricity Application of an electric field causes the charge injection that results in geometrical defects on the symmetric organic molecular structure and exhibit a lower band gap E_g [15] according to figure 1.1 The charge carriers move along the structure and the attraction between the carriers result in excitons formation with a possibility to emit light as photons[8,9]

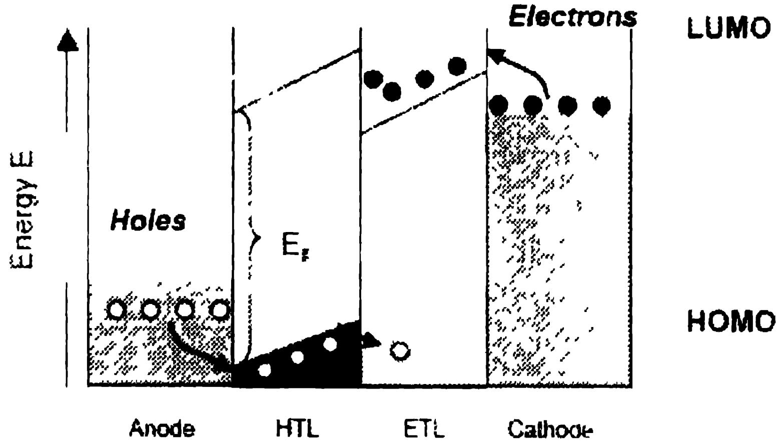


Figure The organic p-n junction in a double-layered device

The excitons are either in singlet or in triplet-states according to the Pauli's principle[16]. The exciton will form two new energy bands inside the band gap. Upon relaxation of the exciton, heat and photons will be emitted with an energy set by the

energy difference between the energy bands that represent the exciton[13] The singlet-state is regarded as the light forming state, while triplet-state is non-allowed transition and decay thermally In some special cases the triplet-state produces light as well[8]

The backbone of the organic materials is made up of strongly localised bonds between the carbon atoms The conductivity is enabled though conjugated π bonds The length of the conjugation set certain characteristics of the molecule The conjugation length defines the length where the electron is free to move within Naturally, small molecules tend to have short conjugation length, while longer conjugated molecules, polymers, may have a longer conjugation length Longer conjugation length results in a smaller band gap It is therefore easier to produce red light with conjugated polymers compared to small molecules, and consequently small molecules can more easily produce blue light[17]

If the conjugation length of a molecule increases to infinity, the band gap reduces to high extent and the electrical conductivity of the material rises quite sharply This can be achieved by doping, i e introducing ions to the conjugated molecules

1.3. Device Architectures

Mono-layered Device [10,14,18,20]

An organic light-emitting device consists of one or more semiconducting organic thin films sandwiched between two electrodes -one of which must be transparent. A simplified schematic of a typical OLED is shown in figure 1 2 Indium tin oxide (ITO) is utilized as the transparent anode and an evaporated metal is utilized as the cathode The device is fabricated by sequentially depositing the organic thin films followed by a

shadow mask defined thin metal cathode onto a transparent conducting ITO coated substrate such as glass or a flexible plastic When a forward bias is applied, injected electrons and holes recombine in the organic layer to generate light Also shown in figure 1.2 is the structure of PPV, the representative material from one of the category of organic semiconductors used in fabrication of OLEDs, a high molecular weight material (polymer)

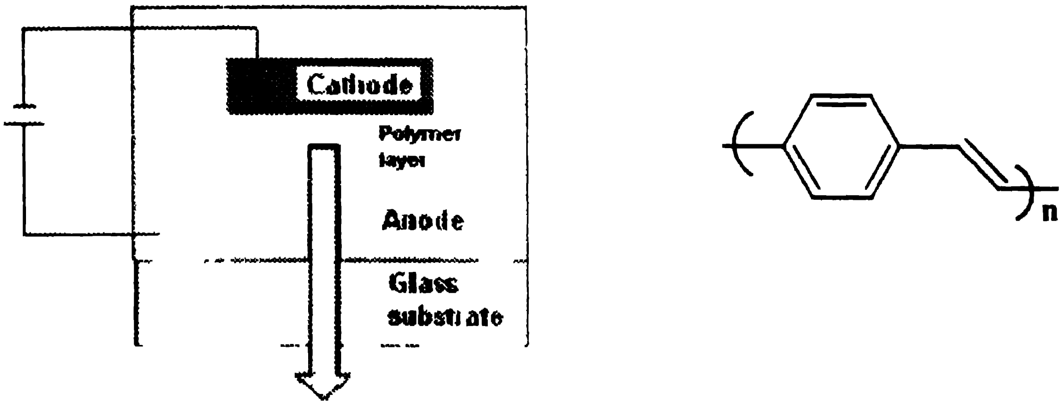


Figure 1 2 Cross section schematic of a typical mono-layer organic light-emitting device Indium tin oxide (ITO) is the anode and a low work function metal is the cathode Typical organic layer thickness is nearly 100 nm Shown to the right is a model polymer poly (p-phenylenevinylene) or (PPV)

The double-layered device[5,18,21]

A minimisation of the energy barrier between the electrodes and the organic material is another approach to enhance the injection of the carriers The mono-layered device is then upgraded to a double-layered device Instead of one organic layer, two layers, a hole transport layer (HTL) and an electron transport layer (ETL), are placed between two electrodes according to figure 1 3 By choosing the material according to

their properties like mobility, band gap, and the charge carriers could be injected and transported in an easier manner into the zone where an emission of light takes place

The energy levels of the materials become more matched to the specific electrode and result in improved equilibrium of the currents of holes and electrons in double layered device The electric field could consequently be decreased, which increases the efficiency and lifetime of the device The difference in energy levels between the two organic layers creates a potential barrier at the interface The barrier confines the holes and electrons and contributes to an increased recombination probability

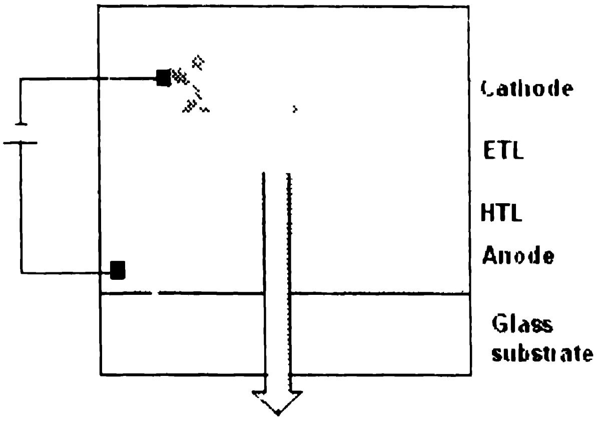


Figure 1 3 Cross section schematic of a typical double layer organic light emitting device

Multi-layered Device [8 11 19 22]

Initially when first organic light emitting diode was discovered in 1987 it was thought that it would be the simplest alternative to inorganic LEDs But as time elapsed and the field expanded a little, it was found that the single layer devices and even the double layer devices are not as efficient as the commercially available inorganic LEDs In case of single layer devices due to unmatched energy levels of cathode and anode with

organic layer, electrons and holes injection from cathode and anode respectively were found difficult due to the potential barrier at interface therefore a poor recombination of holes and electrons and so the radiative decay of excitons. The efficiency was found not to exceed to 25% on the basis of statistical calculations. The recombination in the organic layer caused formation of singlet and triplet states. Since ground state is the singlet state, only singlet to singlet transition is allowed by selection rules therefore singlet excitons decay radiativily while triplet exciton decay by non-radiative process. To improve the efficiencies other routes were also tried. Application of polymers as emitting layer was one of the advanced applications that actually started after the report by Burroughes et al. in 1990.

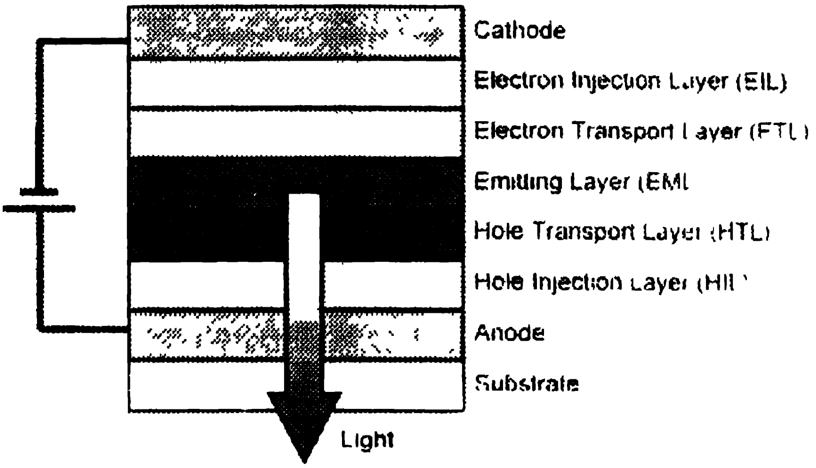

Cathode
Electron Injection Layer (EIL)
Electron Transport Layer (ETL)
Emitting Layer (EML)
Hole Transport Layer (HTL)
Hole Injection Layer (HIL)
Anode
Substrate
Light

Figure 1.4 Cross section schematic of a multi-layer organic light-emitting device[17]

Problem cannot be sorted out just looking into myopically. Some problems like charge injection, carrier mobility, band gap and blocking of holes and electrons from

keeping out of emitting layer should also be given importance For better performance of the diodes, multi-layered device could be fabricated using some useful layers like electron injection layer (EIL), electron transport layer (ETL) hole transport layer (HTL), hole injection layer (HIL) and anode and cathode of appropriate band gap

1.4. Device Physics and Materials

Organic light emitting devices operate on a phenomenon known as electroluminescence Electrically injected carriers recombine to generate light[9] The energy level diagram of a typical single layer polymer based light emitting device (PLED) is shown in figure 1 5 The device utilizes nearly 100 nm thick layer of poly (p-phenylenevinylene) (PPV) as the electroluminescent material with an ITO anode and calcium cathode When the positive voltage is applied to ITO electrode and negative voltage to the calcium electrode[18], electrons are injected from the cathode into the lowest unoccupied molecular orbital (LUMO) of the polymer and holes are injected from the anode into the highest occupied molecular orbital (HOMO) of the polymer[10-23]

Thus, the electrons must overcome the barrier between the Ca Fermi level and the LUMO level of the polymer Low work function metals such as Mg or Ca are typically used to minimize this barrier and provide for an ohmic contact Similarly, to ensure ohmic injection of holes from the ITO Fermi level into the HOMO of the polymer, the ITO may be treated in various ways (*e g*, exposure to an ultraviolet-ozone cleaning) to lower its Fermi level After carriers are injected, they drift in the presence of the externally applied electric field by hopping from molecule to molecule to the opposite electrode[24] Due to the intrinsically low mobilities in these materials, the injection and drift of carriers require high electric fields (nearly 0 1 MV/cm) Achieving low voltage

operation thus limits the thickness of the organic layers to a few hundred-nano metres. If both charges happen to meet on the same molecule or polymer chain, they may combine to form a molecular excited state known as an exciton. The exciton may then either radiativily decays to generate a photon or thermally decays. To maximize OLED efficiencies, electrons and holes must be easily injected from the contacts and transported through the organic layers to form excitons [25]. These excitons must then have a very high efficiency of radiative decay. Thus in addition to choosing optimised contacts for ohmic injection, conductive materials for low voltage transport, materials with high photoluminescence (PL) efficiencies must be chosen to maximize the probability of radiative decay of generated excitons.

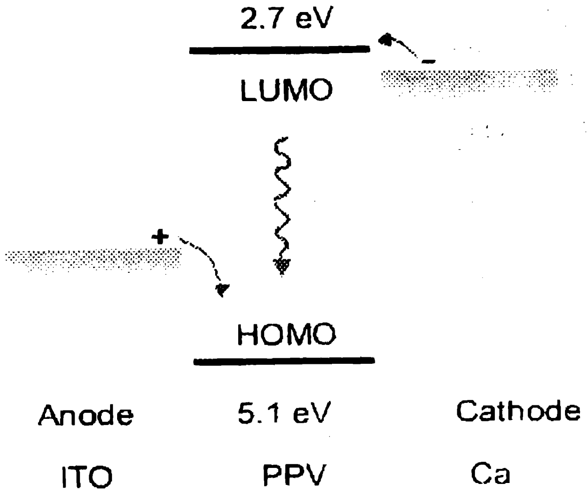


Figure: 1.5. Schematic energy level diagram of a single layer polymer light emitting device fabricated by spin casting a nearly 100 nm layer of poly para-(phenylenevinylene) (PPV) onto ITO and then thermally evaporating a Ca cathode. Shown are the polymer highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Under forward bias, electrons are injected into the LUMO and holes are injected into the HOMO [7].

Now OLEDs are not as simple as it was first fabricated in the laboratory for research purpose. For better light and multi-colour emission a whole range of small molecules like metal chelates and oligomers and polymers, with exciting applications, have been explored. In the near future organic light emitting material will surpass the applications of conventional materials in the field of light emitting diodes. Now a days multi-layer approach is found to be better suited for the best results. Some materials and their applications for different purposes are discussed below.

Substrate- The OLED is built on a substrate that protects the organic layers from moisture and air and therefore prevents eventual degradation. The material is of a rigid or a flexible nature. Simple glass, plastics like PET and silicon back plane can be used[8,10,19].

Anode- A transparent anode is the most suited material so that the radiated light can leave the device. Indium Tin Oxide (ITO), material with high work function, is being used for this purpose because it is completely transparent within visible range of light[9]. Some doped polymers like CSA-PANI[26] has also been applied as anode in OLEDs.

Cathode- The cathode is a low-work function metal. Some widely used metals as cathode are calcium (Ca), and magnesium (Mg)[9]. Aluminium (Al) and some alloys are often used to inject electrons in the organic layer[19]. An effective cathode injects a large amount of electrons in the light-emitting layer.

Hole Injection Layer (HIL)- An organic p-type HIL at the anode interface controls and enhance the injection of the holes from the anode. The layer has a high mobility of hole, which means a low LUMO, and a low ionisation potential and a high HOMO. These facts lower the barrier between anode and the adjacent organic layer and holes can easily be injected into the layer. Some of the materials used for the purpose are copper

phthalocyanine (CuPc), perylenetetracarboxylic-diamine (PTCDA) and poly ethylenedioxy thiophene (PEDOT)[9]

Hole Transport Layer (HTL)- An effective organic HTL needs to transport hole effectively to the light-emitting zone and in some cases also function as charge blocking layer for electrons The material of the HTL requires therefore a high mobility of the hole but also a low ionisation potential The materials used for the purpose are the diphenyl diamines (TPD), NPD, PPV and PPP etc[7]

Electron Injection Layer (EIL)- As for the holes, an organic injection layer for the electrons EIL is used to help the electron from the cathode to the ETL For a high mobility, a high HOMO and low LUMO is required An improvement of the conductivity of the layer can be achieved by doping the host with low-work function metal or with reactive metal Better transports of the charge carriers accomplish a lower required electric field, which leads to a more power efficient OLED device The most suitable material used for the purpose is Alq3 [9]

Electron Transport Layer (ETL)- The ETL is an n-type doped organic material that transports the electron An effective material has high LUMO and high ionisation potential The ETL has to match with the HTL to accomplish equilibrium of the amount of charge carriers transported in the EML For this purpose aluminium based organometallic complex like Alq3 is the most suitable material[7]

Emitting Layer (EML)- The main function of the emitting layer is to provide the hole, injected from anode and electron, injected from cathode, to recombine and decay radiativley Materials used are PPVs , PPPs, polyfluorene, ladder polymers, dendrimer and small molecules like metal chelates and oligomers [9]

1.5. Advantages

Organic light emitting diodes are now came out of laboratory trials and since last few years they have been applied in the microelectronic gadgets to enhance efficiency and lifespan of the gadget The miniaturization of the electronic gadgets in future will be possible The most advantageous thing going to happen that the shape and size of illumination system will change dramatically[10] Some of the most important advantages that will lead the development of the OLEDs as one of the feasible technologies are-

Enhanced brightness, contrast and low glare[19],

- Improved colour variation and resolution
- Reduced cost on manufacturing and power consumption [10]
- Ultra-light weight and ultra-thin devices are possible[22],
- Wide viewing angle nearly 160^{0} [10],
- Wide operating temperature range and inherent ruggedness[19],
- Large area coatings[19],
- Device can be fabricated in any shape[19],
- Variable pixel size from displays to large area illumination [19],
- Low operating voltage (2 V) and fast switching speed[27],
- Almost two-dimensional light source is possible,
- No back light required for video display,
- Can be spin coated on the substrate[1] and
- Ink-jet printing technology possibly will reduce the cost of OLEDs so effectively that it could be affordable to general public[19]

1.6. Inhibiting Factors

Some of the inhibiting factors that are the concern of the general applications of OLEDs are short operational and shelf life, stability at high brightness levels, low device efficiency[6]. Complex device structure may affect the cost of manufacturing[15]. Uniformity of the coating for large area lighting sources is the main concern.

1.7. Advances and Applications

We have only begun to imagine what OLED technology can create in the way of products, applications, job creation and new markets. The technology will not only improve existing methods of illumination but will create entirely new lighting product possibilities. OLEDs will create new markets where distributed sources of light can be applied, or are even desirable.

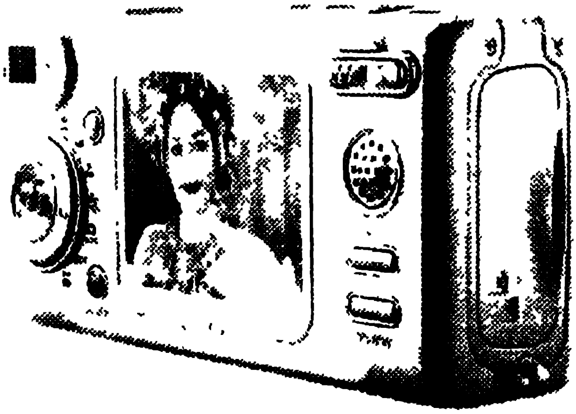


Figure 1.5 A Kodak digital camera displays picture using AM-OLED matrix

The focus of the OLED industry is now on the application in displays. The first application other than in display will probably be backlighting (such as LC displays), and on a large scale, for location maps in shopping malls, advertising signs etc. Lightweight,

thinness and flexibility will allow different mounting options, which in turn will motivate a shift from the conventional light bulbs One can envision that ceiling or wall panels made of OLEDs can light commercial buildings in future The desired luminescence will vary according to the applications [28,35]

Some recent applications that have been realised during last few years are-

-Pioneer introduced the first commercially available OLED based display in 1997 It was a passive matrix display used for car radio faceplates [35,36]

-Small molecules based displays were also found in Motorola cellular phones by 2000

-More recently, the first commercially available polymer based LEDs have been sold in a simple passive matrix scheme as displays in MP3 players made by Delta Optoelectronics [10]

-In a well published Phillips electric razor displayed as prominently as James Bond's newest gadget in the movie "Die Another Day" [10]

-Kodak has just recently announced the first commercially available AM-OLED display used in digital cameras [10,29,63] as shown in figure 1 6

Some futuristic applications of OLEDs are- large scale displays, "smart panels", ultra-light weight wall hanging TV monitors, large screen computer monitors, light panels for residential and commercial buildings, light emitting wallpapers, lighting for advertising sign boards, office windows, walls and partitions that could be used as the computer screens, colour changing lighting panels, and walls for home and office, active clothing etc all at a low cost[28,35]

Synthetic Routes: Semiconducting Polymers

2.0. Introduction

Conjugated polymers combine the physical properties of polymers like low specific weight, processability, solubility, tuneable mechanical properties, flexibility etc with those of semiconductors to obtain unique and novel material with exciting applications[-] Examples of such applications are large-area flexible polymer light emitting diodes (PLEDs) that can emit light virtually in any part of the visible spectrum, all-polymeric field effect transistors (FETs) that give access to high-tech, but low cost plastic electronics and polymers with metallic conductivity for the simple fabrication of conductive films e.g. for electromagnetic induction (EMI) shielding or antistatic applications[4-13] Besides their attractive material properties, the power of conjugated polymers is to be found in the ease to manipulate their chemical structure This allows the fabrication of materials with tailor-made electronic and mechanical properties

Conjugated polymers are organic semiconductors that with respect to electronic energy levels hardly differ from inorganic semiconductors Both have their electrons organized in bands rather than discrete levels and both have their ground state energy bands either completely filled or completely empty The band structure of a conjugated polymer originates from the interaction of the π orbital of the repeating units through the chain Interaction between the π-electrons of neighbouring molecules leads to a three-dimensional band structure[17]

Analogous to semiconductors, the highest occupied band, which originates from the HOMO of a single repeat unit, is called the valence band, while the lowest unoccupied band, which originates from the LUMO of a single repeat unit, is called the conduction band[18] The difference in energy E_g between these levels is called the band

gap. Since π-conjugated polymers allow virtually endless manipulation of their chemical structure, control of the band gap in semiconducting polymers is very useful way to exploit for further applications.

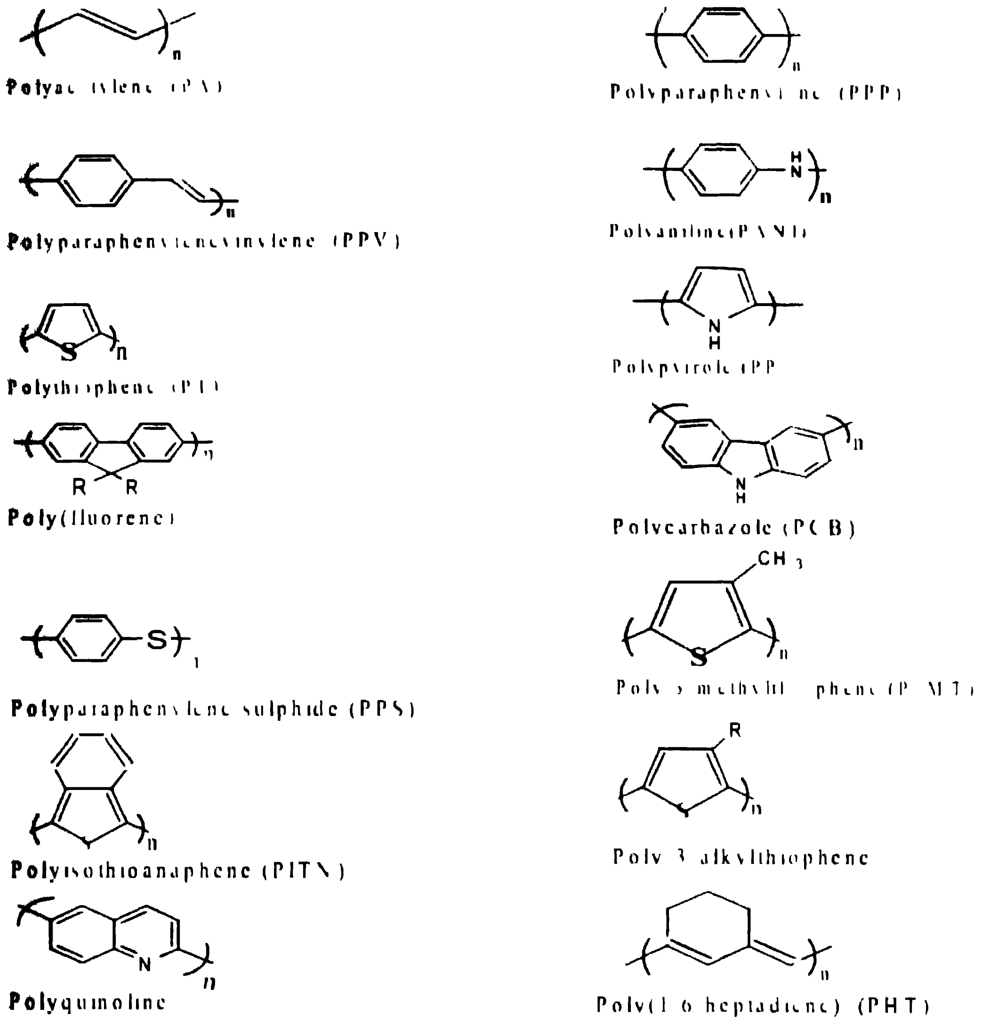


Figure 2.1 Molecular structures of some representative semiconducting conjugated polymers

Understanding these fact polymer chemists can synthesize polymers of the desired length and desired properties For this purpose it is required to know some well-known

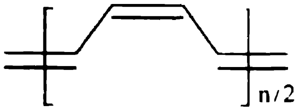
synthetic routes to semiconducting polymers As all semiconducting polymers have extended π-conjugated backbone Their studies can, mainly, be divided into three parts[17] namely

1. Synthetic routes to hydrocarbon based polymers,
2. Synthetic routes to polymers with heteroatom in main chain
3. Synthetic routes to oligomers

In the first part, the study of synthetic routes to hydrocarbon based polymers synthesis polyacetylene (the first polymer which was found electrically conducting and generated much interest among academicians), synthesis of poly(p-phenylene) (PPP) and synthesis of poly(p-phenylenevinylene) (PPV) will be covered in detail In the second part, the synthetic routes to polymers with heteroatom in main chain synthesis of polyaniline, and polythiophene will be covered And finally in the third part, synthetic routes to oligomers, synthesis of p-sexiphenyl will be covered Some representative semiconducting polymers are given in the figure 2 1

2.1. Synthetic Routes to Hydrocarbon Based Conjugated Polymers

2.1.a. Polyacetylene



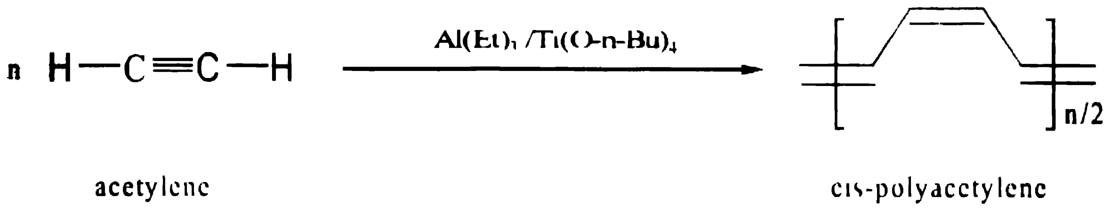
Polyacetylene

Polyacetylene is the simplest, the most prominent and well-studied hydrocarbon based conjugated polymer[2] The first report on acetylene polymers dates back to 19th century Cuprene a highly cross-linked and extremely irregular product of acetylene,

polymerises in the presence of copper containing catalyst is the typical example. Polyacetylene was first prepared as a linear high molecular weight, conjugated polymer with highly regular structure in 1958 when Natta et al. polymerised acetylene in hexane using $Al(Et)_3/Ti(O\text{-}Pr)_4$ as the initiator system. It was obtained as an air sensitive, infusible and insoluble black powder. For many years nobody took interest in polyacetylene.

Shirakawa's Route:

A new phase in the polymeric materials began in the 1970s when Shirakawa and co-workers developed a simple method for preparing film samples, which on treatment with oxidizing agents, such as halogens or AsF_5, exhibited significant electrical conductivity[14-23]. Shirakawa's route to polyacetylene is an extension of the work first described by Natta et al. The polymerisation reaction is carried out at the surface of a solution of the initiator system in an inert solvent[17-19]. The initiator concentration used was thousand times to that was used by Natta's solution phase work.

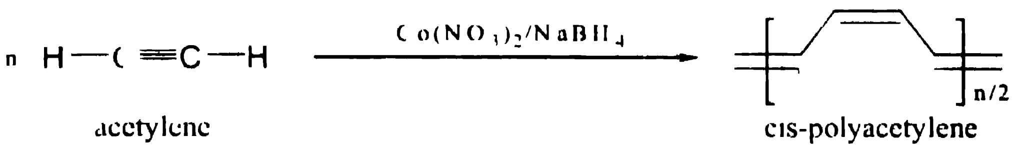


Scheme 2.1 Shirakawa's route to polyacetylene

The ratio of catalyst Al/Ti was taken 3.5 to 4 and the product obtained was mainly cis-acetylene. Later Baker et al. found that if Al/Ti ratio is kept unity and omitting the catalyst-aging step, the product obtained was purely trans-polyacetylene.

Luttinger's Route:

In 1980 Enkelmann et al note that powdered polyacetylene specimens prepared by traditional methods possessed properties which were essentially the same as those of the material produced by Shirakawa's method Such powders could be suspended in an inert solvent and application of the suspension to a suitable substrate followed by evaporation of the solvent gave thin films of polyacetylene. Later, Enkelmann et al discovered that the best results are obtained using $Co(NO_3)_2$/ $NaBH_4$ as the initiator system , system of this type contains salts and complexes of group 10, 11 or 12 metal together with a hydride reductant were first used by Luttinger twenty years earlier[17,19]



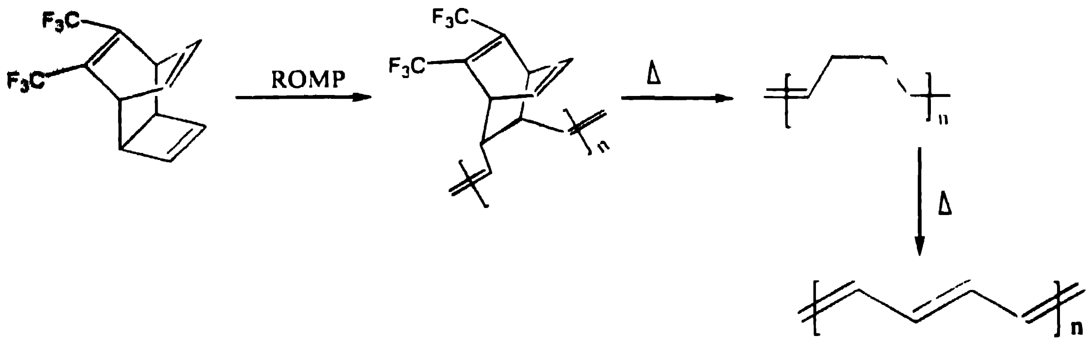
Scheme 2.2 Luttinger's route to polyacetylene as developed by Enkelmann

In a typical experimental procedure ethanol is saturated with gaseous acetylene, and sodium borohydride followed by cobalt nitrate are added After several hours' reaction at room temperature black flakes of polyacetylene precipitated By lowering the reaction temperature to $-30\ ^{0}C$ the formation of a predominantly cis-structure is favoured.

The main advantage of Luttinger's catalyst over that developed by Shirakawa is that it allows the polymerisation reaction to be carried out even in the presence of water and air.

Precursor-polymer Route:

The inherent insolubility and infusibility of polyacetylene coupled with its sensitivity to air imposes a barrier to the processability of the polymer To eradicate this problem an approach to synthesize soluble prepolymers, which can be thermally converted to polyacetylene, was first described by Edwards and Feast

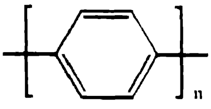


Scheme 2 3 The precursor route to polyacetylene

In this approach, the initial monomer, 7,8-bis(trifluoromethyl)tricyclo[4 2.2.0] deca-3,7,9-triene is readily prepared by the thermal cycloaddition reaction between hexafluorobut-2-yne and cyclooctatetraene The polymerisation reaction is carried out in the presence of ring opening metathesis polymerisation initiators, such as $WCl_6/SnMe_4$, which act only on the strained four member ring to form a high molecular weight precursor polymer which is soluble in common organic solvents and can be purified,

characterized and processed by conventional methods On heating, the prepolymer can be easily and conveniently converted to polyacetylene with the evolution of 1,2-bis(trifluoromethyl)benzene[37,39]

2.1.b. Polyphenylene

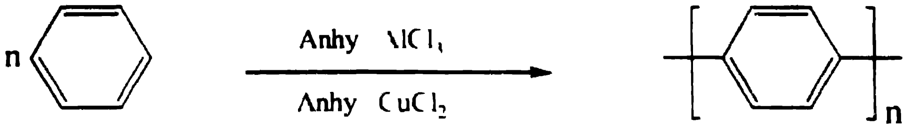


Polyphenylene

Aromatic hydrocarbon in the p-polyphenylenes have attracted considerable attention because of their good thermal stability, high melting points, insolubility, electronic configuration, the interest in them as moderators in nuclear reactors and now candidate for electroluminescent material[42] Polyphenylene is the representative polymers of all the benzene ring coupled polymers It is also well-studied polymers next to polyactylene Earlier, p-polyphenylenes were prepared by classical methods like Ullmann coupling, Fittig reaction and the Grignard synthetic route[37] But for better results and its use as electroluminescent materials oxidative coupling, organometallic coupling, dehydrogenation of polycyclohexylenes and some others are prominent methods that can be studied here

Oxidative Coupling:

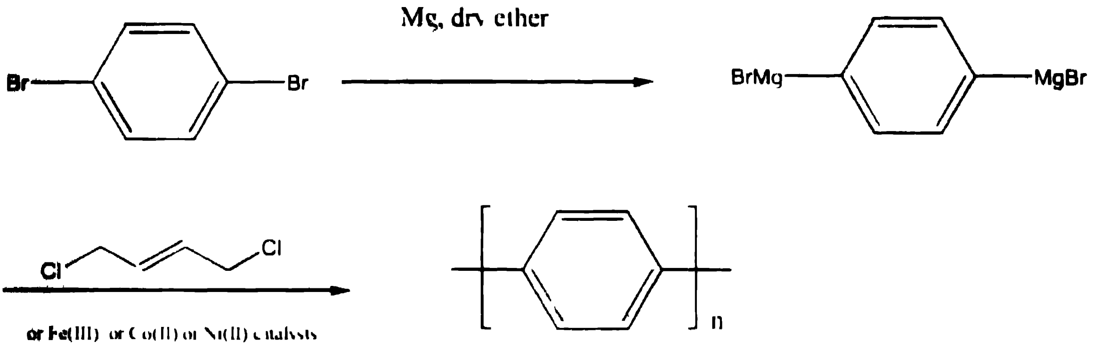
The most commonly employed method for the preparation of polyphenylenes involves the oxidative coupling of substituted and unsubstituted benzene via treatment with a Lewis acid catalyst/oxidant system In 1963 Kovacic and Kyriakis synthesized polyphenylenes by stirring benzene, anhydrous $AlCl_3$ and anhydrous $CuCl_2$ for 2 hours at temperatures between 25 ^{0}C and 35 ^{0}C [37,43]



Scheme 2.4 The oxidative route to poly(p-phenylene)

The reaction is believed to involve an initial one-electron oxidation of benzene to its radical cation with several benzene molecules to give an oligomeric radical cation. A second one-electron oxidation, followed by loss of two protons aromatises the terminal rings, and oxidative re-aromatisation of the dihydro structures by $CuCl_2$ yields the polymer.

Organometallic Coupling:

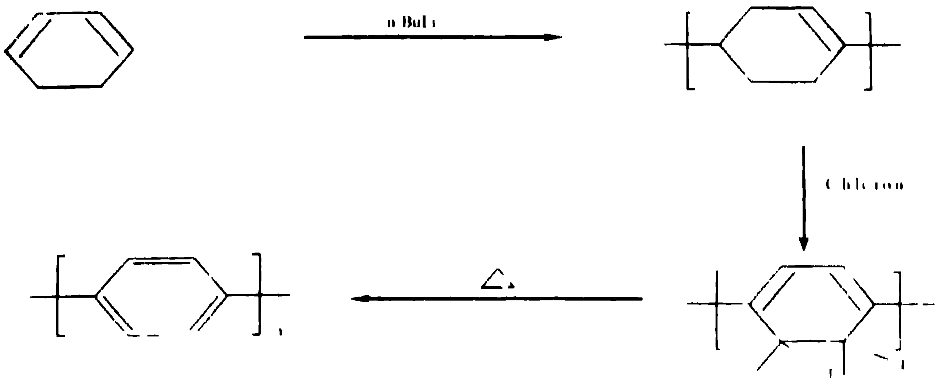


Scheme 2.5 The organometallic coupling route to poly(p-phenylene)

The preparation of polyphenylenes via the coupling of Grignard reagent is proved more suitable. Thus the coupling of the mono-Grignard reagent of dihalobenzene in the

presence of organometallic or organic promoters has been used for the synthesis of a range of para and meta substituted polyphenylenes [17]

Dehydrogenation of Polycyclohexyene:

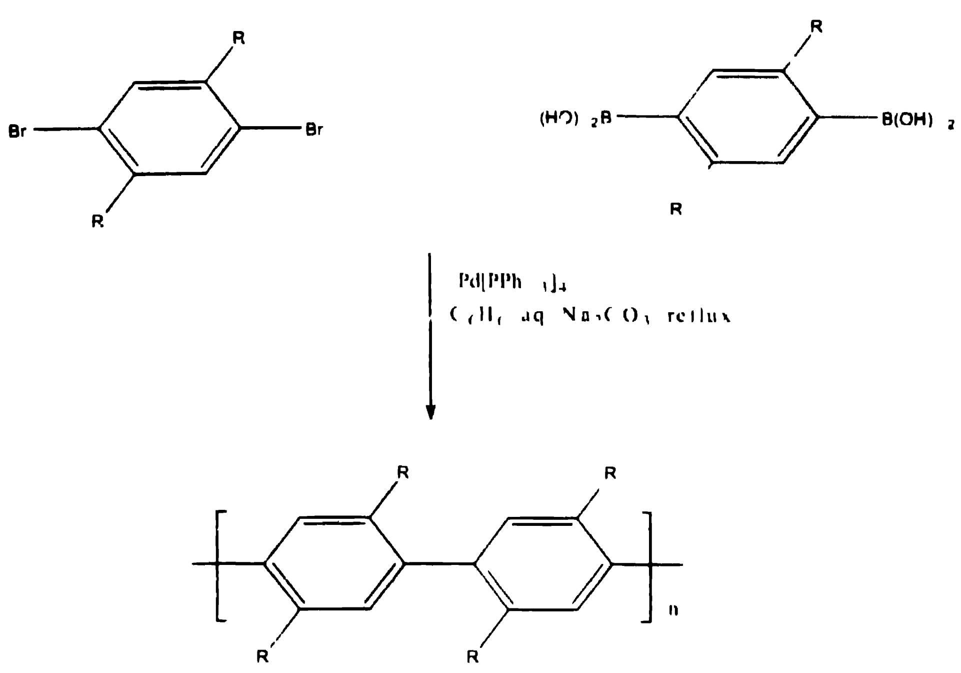


Scheme 2.6 The dehydogenation of polycyclohexyene route to poly(p-phenylene)

The polymerization of 1,3-cyclohexadiene in the presence of various Zigler type initiator system or n-butyllithium yields poly(1,3-cyclohexadiene). Dehydrohalogenation of this precursor polymer with chloronil or via halogenation/pyrolysis gives polyphenylene[17]

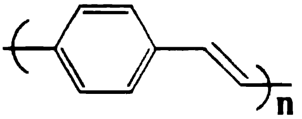
- **Yamamoto Route:**

The soluble substituted polyphenylenes with high molecular weight are obtained by the Palladium catalysed Yamamoto coupling reaction This reaction is very specific for C-C coupling. By altering the functional groups in the reactant even the small chain length oligomers can be obtained [17 44 45].



Scheme 2.7 The Yamamoto coupling route to poly(p-phenylene)[45]

2.1.c. Poly(p-phenylenevinylene)s



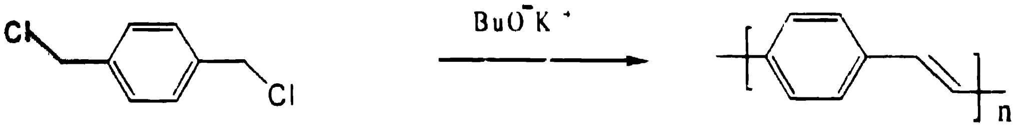
Polyparaphenylenevinylene

Poly(p-phenylenevinylene)s (PPVs) possess a chemical structure which is intermediate between that of polyacetylene and polyphenylene. Oriented PPV is highly crystalline, mechanically strong and environmentally stable[47, 48]. A number of approaches have been developed for the synthesis of these polymers and its analogues. The synthetic routes of poly(p-phenylenevinylene) (PPV) can be studied under following two heads: first way is Direct Approach, in which PPV is obtained as a amorphous

intractable solid and the second way is Precursor Approach, in which PPV is first obtained as polyelectrolyte solution later the film of this precursor is converted into PPV on thermal annealing[46]

Direct Approach

Gilch Route:

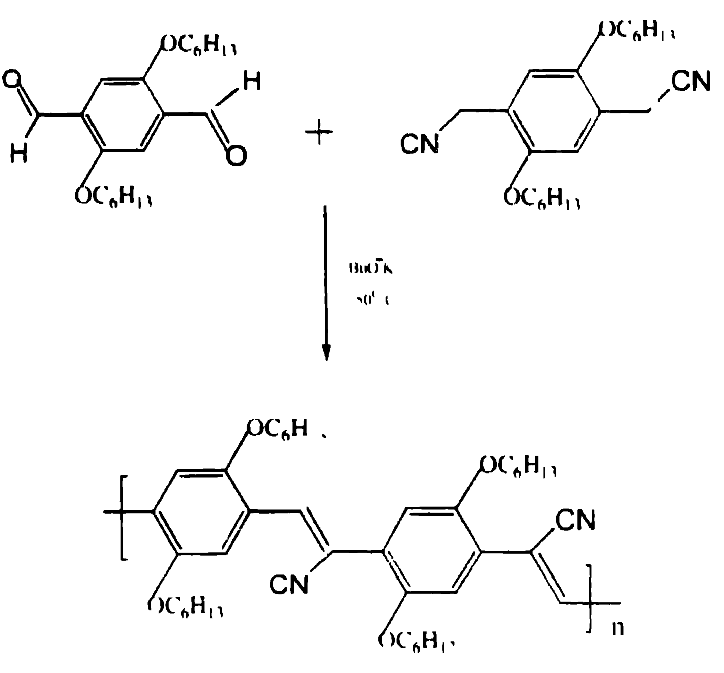


Scheme 2.8 Gilch route for the synthesis of PPV

One of the earliest report on direct synthesis of PPV dates back to 1966, when **Gilch** et al prepared PPV by adding excess potassium tert butoxide to p-xylenedichloride This method, widely known as Gilch route yielded an insoluble polymer[7, 37, 46, 47]

Knoevenagel Synthetic Route:

Harhold et al used an approach to make a special class of electron deficient PPVs-cyno PPV The limitation of this method is that it always generates PPV derivatives in which the cyno groups lay on the benzylic carbons of every alternate phenyl ring[7, 7, 46, 50]

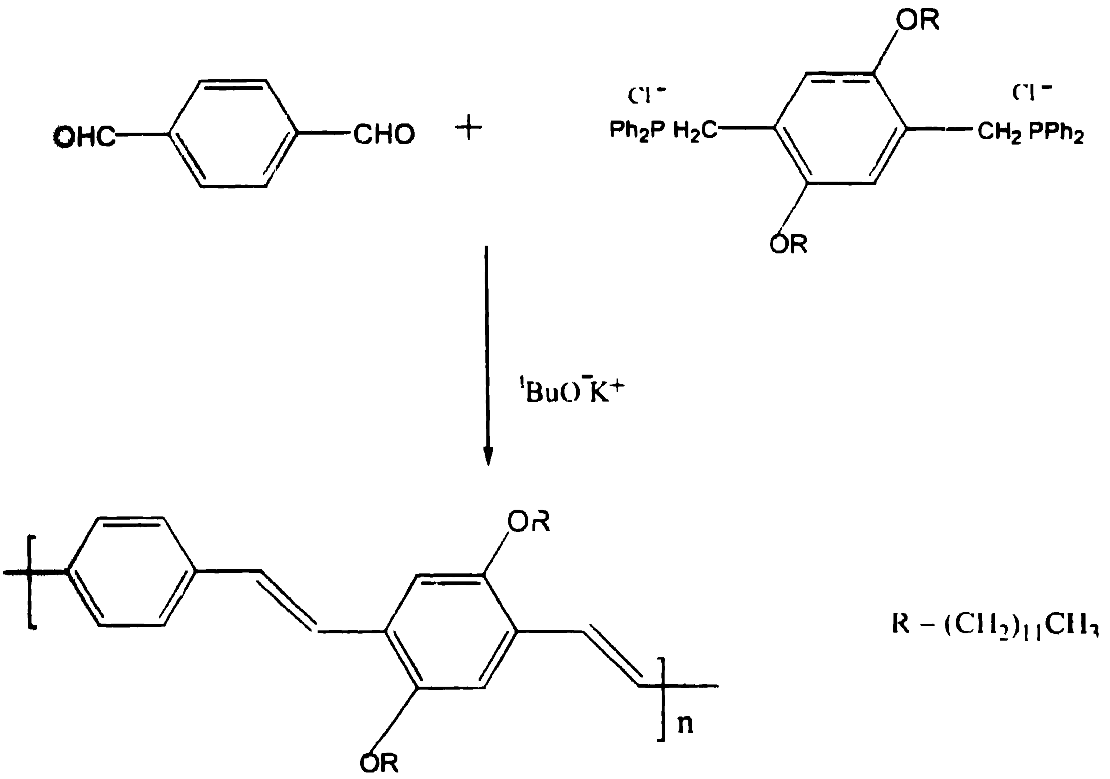


Scheme 2.9 Condensation polymerization of cyano-PPV via Knoevenagel route[49]

Wittig Synthetic Route:

Terephthalaldehyde is reacted with the triphenyl phosphonium salt of bis-(chloromethyl)benzene derivative to generate PPV of high molecular weight[7, 37, 46]. Whereas terephthalaldehyde yields completely conjugated PPV, using an aliphatic dialdehyde as a comonomer results in PPV of well-defined conjugation length, in which the aliphatic linker separates the conjugated segments[51].

Other reactions like Heck reaction, electrochemical polymerization of α, α, α', α'-tetrabromoxylenes, McMurray deoxygenation of aromatic aldehyde[52], metal catalyzed arylation of ethylene, ring-opening metathesis polymerization, etc have been successfully utilized to synthesise PPV



Scheme 2.10 Wittig polycondensation for PPV synthesis

Precursor Approaches

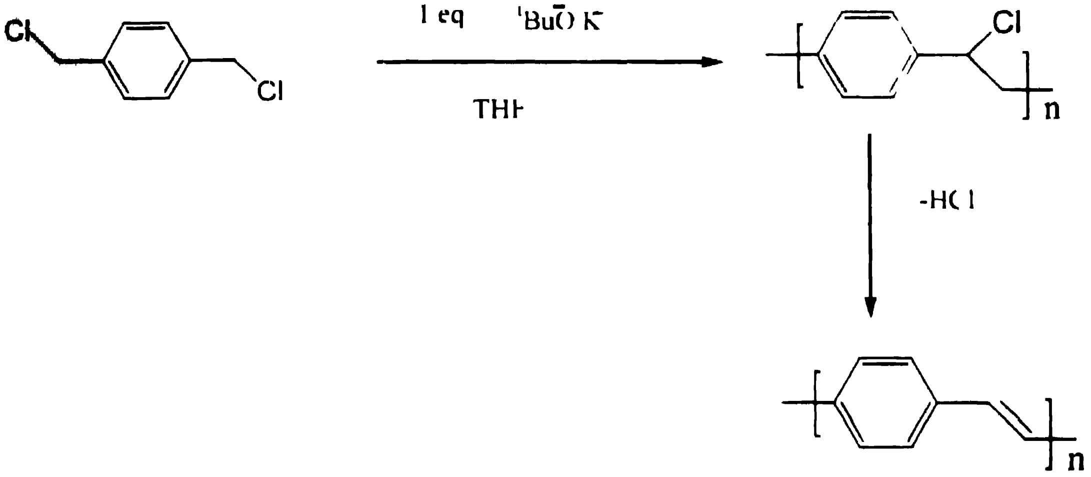
The precursor approaches for the synthesis of PPV and its derivatives have been more widely used than the direct methods for most of the polymers. Through precursor routes water/organic solvent soluble derivatives of PPV can be prepared. Two most important precursor routes towards PPV are [46]-

Halo precursor route

Wessling's Sulphonium precursor route

Halo Precursor Route:

A modified Gilch route has been used as a halo precursor route, in which, one equivalent of a strong base is added to the α, α'-dihaloxylene derivatives in order to get the halo-precursor polymer (Scheme 2.11) This can be purified, cast into thin film on a suitable substrate and heated to 220-250 °C to yield the conjugated polymer [4]

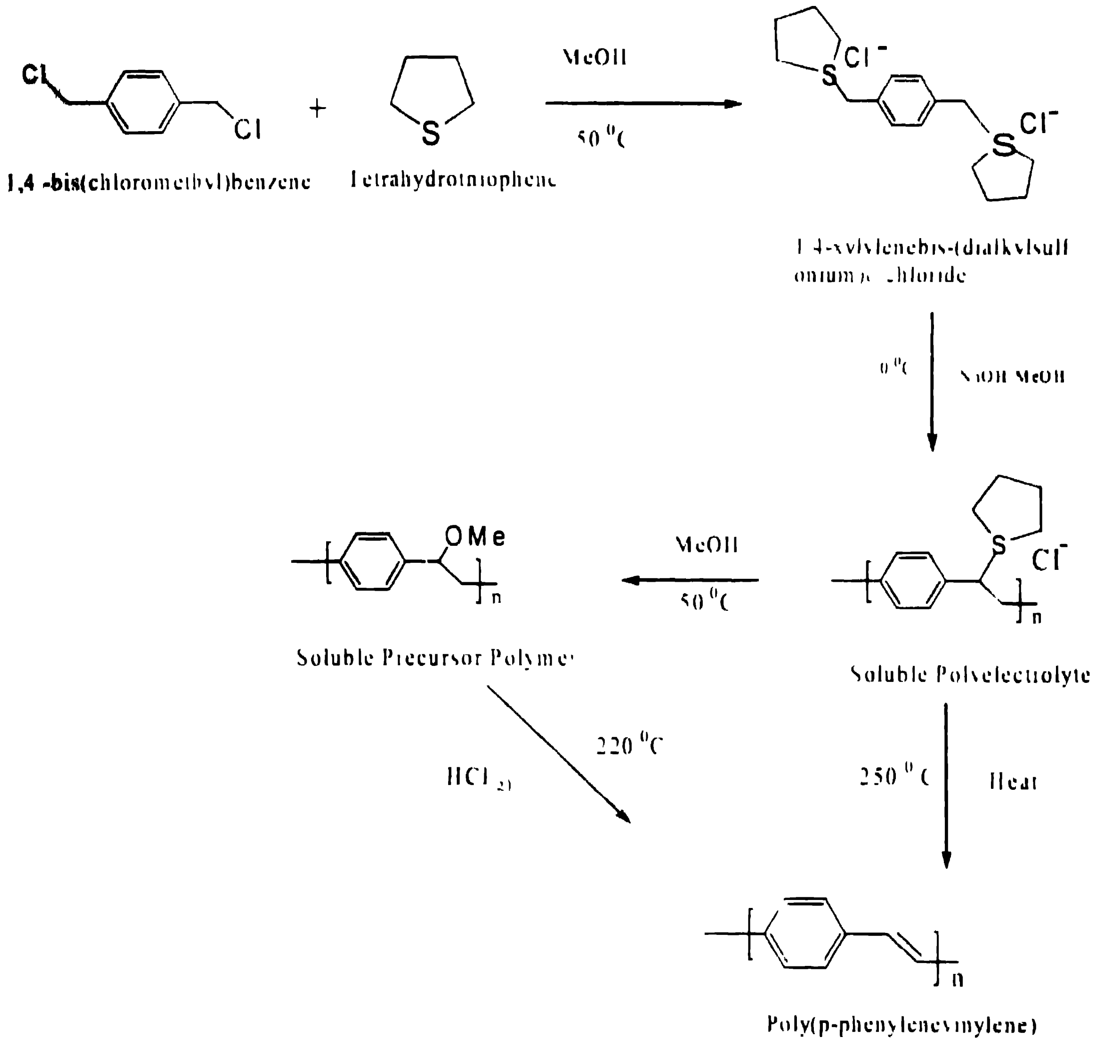


Scheme 2.11 Chloro precursor route to PPV [4]

Even though the initial reports claim the isolation of the halo-precursor polymer by precipitation into methanol, later studies have revealed that the halogen group is rapidly substituted by methanol in dialkoxy-substituted precursors On the other hand, this facile substitution apparently doesn't take place when the phenyl ring is unsubstituted or has only one alkoxy unit. Precipitation of the solution of the precursor into a weakly nucleophilic solvent like iso-propanol afforded the chlorine precursor polymer

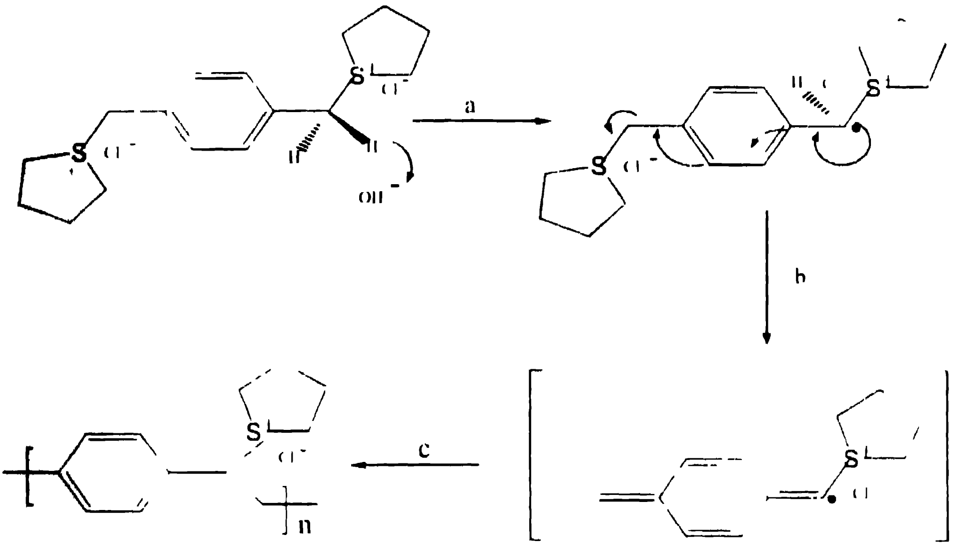
Wessling's Sulphonium Precursor Route:

This is the most widely used precursor approach for the synthesis of PPV. 1,4-xylylenebis-(dialkylsulphonium)dichloride was readily polymerized using NaOH in water or methanol. This gives rise to the Wessling's polyelectrolyte, which is soluble in methanol and water. Evidences for both nonradical mechanism and radical mechanism have been reported[7,15,37,53-55].


Cl
Cl
1,4-bis(chloromethyl)benzene
+
S
Tetrahydrothiophene
MeOH
50 °C
S
Cl⁻
S
Cl⁻
1,4-xylylenebis-(dialkylsulfonium) chloride
0 °C
NaOH MeOH
S
Cl⁻
n
Soluble Polyelectrolyte
MeOH
50 °C
OMe
n
Soluble Precursor Polymer
220 °C
HCl (g)
250 °C
Heat
n
Poly(p-phenylenevinylene)

Scheme: 2.12. Wessling's sulphonium precursor route to PPV[46]

This precursor polymer, after dialysis against water over 3 days, is devoid of low molecular weight impurities. The polymer can be dissolved in methanol and cast as such to get a thin film, which, upon heating to 150-180 °C, undergoes elimination by the loss of tetrahydrothiophene and HCl to yield the conjugated polymer, PPV. The sulphonium group in the Wessling polyelectrolyte is readily substituted by nucleophiles such as methanol, to give a neutral, organic-soluble precursor polymer. The methoxy precursor too undergoes elimination when heated to nearly 220 ^{0}C in the presence of dry HCl gas, to give the conjugated polymer. The modified Wessling route is shown in scheme 2.12.



Scheme: 2.13 Schematic of the mechanism of Wessling's sulphonium percursor route to PPV[46]

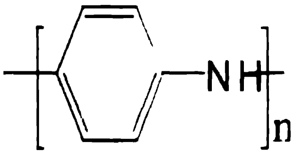
The basic mechanism for the polymerization via the sulfonium precursor route is given in scheme 2.13. The key steps involved in the mechanism are (a) abstraction of the benzylic methylene proton by the base to generate a carbanion, (b) 1,6-elimination of one

molecule of tetrahydrothiophene and chloride ion to generate a quinodimethane intermediate and (c) 1,6-polymerization of the unstable quinodimethane yielding the precursor polyelectrolyte The Gilch polymerization too is believed to follow a similar mechanism [37,46,54]

Initial studies confirmed that several side-reactions occurred, leading to uncontrolled microstructure of the precursor polymers It was observed that the halide counter-ion acted as a nucleophile, replacing the sulphonium group, giving rise to partially halo-substituted precursors In non-cyclic sulphonium salts, the elimination of methyl halide was also observed, leading to the sulphane-precursor polymer Using a cyclic sulphide like tetrahydrothiophene circumvented the latter problem

2.2. Synthetic Routes to Polymers with Heteroatoms in Main Chain

2.2.a. Polyaniline



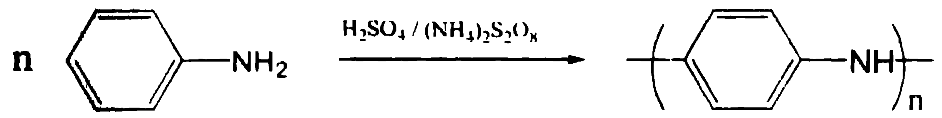
Polyaniline

Polyaniline also known as aniline black was first prepared in 1834 and has been the subject of intensive research ever since In the 1980s the conducting properties of polyaniline were recognized and the number of papers dealing with this conducting polymer grew rapidly The main reasons for this growth, besides the scientific interest, are the low cost of aniline, the relatively easy production process and the stability of the conducting forms [56]

Chemical/ Electrochemical Oxidation route:

Oxidation of aniline is the most widely employed synthetic route to polyaniline and can be performed either electrochemically or chemically. The reaction is usually carried out in acidic media. The electrochemical method was originally developed by Lethcby as a test for the determination of small quantities of aniline. The method has been improved ever since and has also been applied to alkyl, alkoxy and dimethoxy substituted anilines, the latter exhibiting conductivity comparable to that of unsubstituted polyaniline

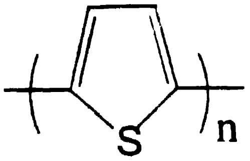
Chemical oxidation is usually carried out in acidic aqueous environments with an oxidizing agent such as ammonium persulphate, but has also been performed in chloroform using tetrabutyl ammonium periodate.



Scheme: 2.14 The electrochemical/chemical route to polyaniline

Alkyl and alkoxy substituted polyanilines have also been prepared utilizing this chemical method. It has been stated that in polyaniline cross-linking occurs during the electrochemical synthesis due to the potential applied. However, non-oxidatively synthesized polyaniline, exhibiting the same properties, has a fully linear structure. Cross-linking in polyaniline can also be accomplished when the emeraldine base is heated up to 300 °C [17].

2.2.6. Polythiophenes



Polythiophene

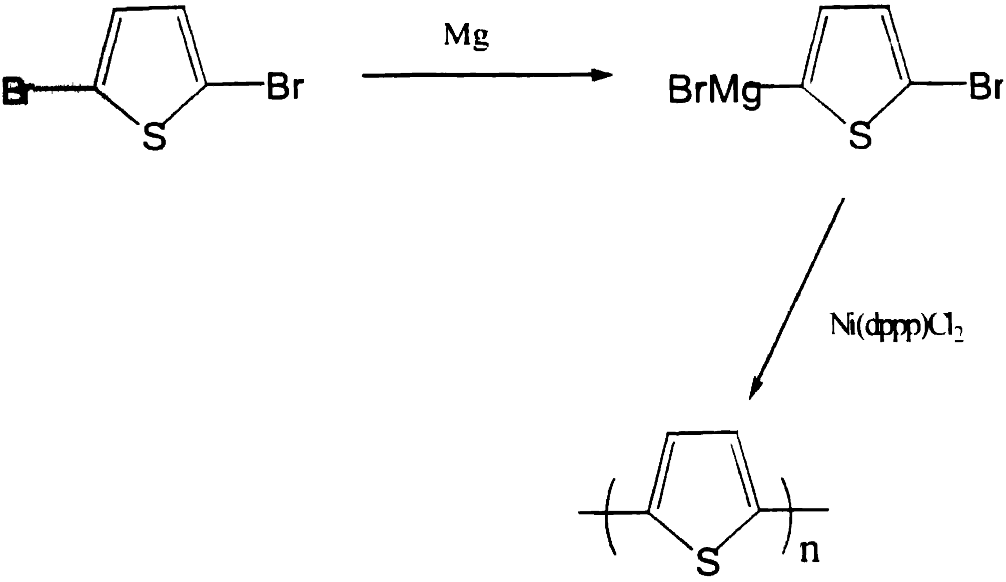
The first polythiophene synthesis was described in 1883 when the purification of thiophene with sulphuric acid yielded a dark insoluble material However, it was not until the early 1980s that any well-defined polymeric material was obtained After the first report of a controlled synthesis by Yamamoto and Lin, using the Grignard-type coupling of 2,5-dibromothiophene, a vast number of articles concerning the synthesis and properties of polythiophenes have been published[57]

Extended π-conjugation in polythiophenes is only possible in polymers with perfectly 2,5-linked repeating units, however, 2,4- and 2,3-couplings as well as hydrogenated thiophene units can also be found in the polymers These structural defects interrupt the conjugation and, as a result, will impair the development of properties related to conductivity and non-linear optics[59]

Polythiophenes, like many other linear polyaromatic compounds, are insoluble in organic solvents due to their rigid backbone This lack of solubility and processability, as well as problems related to the characterisation of polythiophenes, has been overcome by the introduction of flexible side chains at the 3- and/or 4-position Appropriate solubility in common organic solvents has been achieved with an alkyl side chain of more than four carbon atoms at every repeating unit Longer alkyl side chains are required in the case of copolymers with less than one side chain per repeating unit With the introduction of

substituents at the 3-position of polythiophenes a number of different regioisomers are possible, namely head-to-tail (HT), head-to-head (HH) and random configurations

Organometallic mediated synthesis:



Scheme: 2.15. The organometallic mediated synthesis of polythiophene

The nickel and palladium catalysed cross coupling of an aromatic organometallic compound with an aromatic organohalide is a well-known method for the synthesis of oligoheterocycles. Organomagnesium derivatives are most widely employed in polythiophene chemistry. The reaction of 2,5-dibromothiophene with magnesium and subsequent polymerisation using a nickel catalyst was described in 1980, with a reported yield of 40-60% based on 2,5-dibromothiophene. The yields have been improved up to 93% by using 2,5-diiodothiophene, magnesium and Ni(dppp)Cl$_2$ as catalyst [37 39].

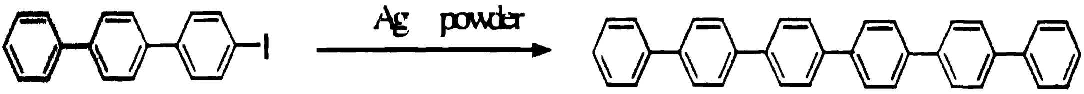
2.3. Synthetic Routes to Oligomers

2.3.a. p-sexiphenyl

Oligomers are the small molecules that contain four to ten monomeric units. These days oligomers have found its place particularly in the field of organic electronics as electroluminescent materials, non-linear optical materials[35] etc. Now a days p-sexiphenyl have been used in OLEDs as blue emitter. It can be synthesize by Ullmann coupling, Kovacic coupling and Suzuki-Murayama coupling methods[37-39]

Ullmann Coupling:

In this method a mixture of 4-iodo-p-terphenyl and silver powder at 330 °C. But in this method effecting condensation is very difficult and yield is also poor[37]. Many other improvements on this method have been reported in literatures.



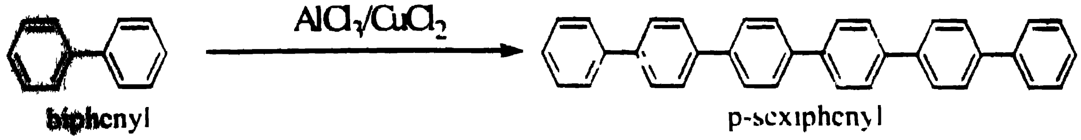
4-iodo-p-phenyl

p-sexiphenyl

Scheme 2.16 Ullmann coupling route to p-sexiphenyl

Kovacic Coupling:

Kovacic et al have succeeded in synthesizing p-sexiphenyl in good yield and high purity by a novel, one-step reaction involving biphenyl and Lewis acid catalyst/oxidant system. Inexpensive, and readily available starting materials are used. Under mild conditions, biphenyl is converted to the trimer-type product on treatment with aluminum



Scheme 2.17 Kovacic coupling route to p-sexiphenyl

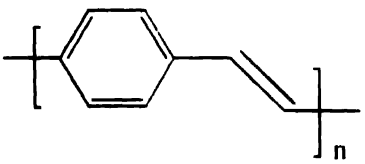
chloride/cupric chloride oxidant system. Minor amounts of higher p-polyphenylenes are also formed, as well as p-quarterphenyl. The product can be isolated by vacuum sublimation[37, 43]

Experimental Works

3.1. Synthesis of Electroluminescent Materials

3.1.a. Synthesis of poly(p-phenylenevinylene)

PPV, one of the conjugated polymers which was first applied in light emitting diodes as early as in 1990, is the highly structured and a green-yellow light emitting electroluminescent polymer. Oriented PPV is highly crystalline, mechanically strong and environmentally stable and these characteristics make it one of the most studied electroluminescent polymers even in recent times



Molecular structure of PPV

Early attempts for PPV synthesis utilized dehydrohalogenation or Wittig condensation reactions, which resulted in the formation of intractable oligomeric powders hence a new way was required to develop and the PPV was prepared via the precursor route. The precursor route involves the preparation of a soluble polymer intermediate that is cast on the appropriate substrate and after thermal treatment is converted to the final product in situ This involves producing a polymer in which the arylene units are connected by ethylene units. The saturated units in the precursor contain a group that not

only solubilises the macromolecule and allows for processing, but also acts as a leaving group, thus affording the unsaturated vinylene units of a fully conjugated polymer

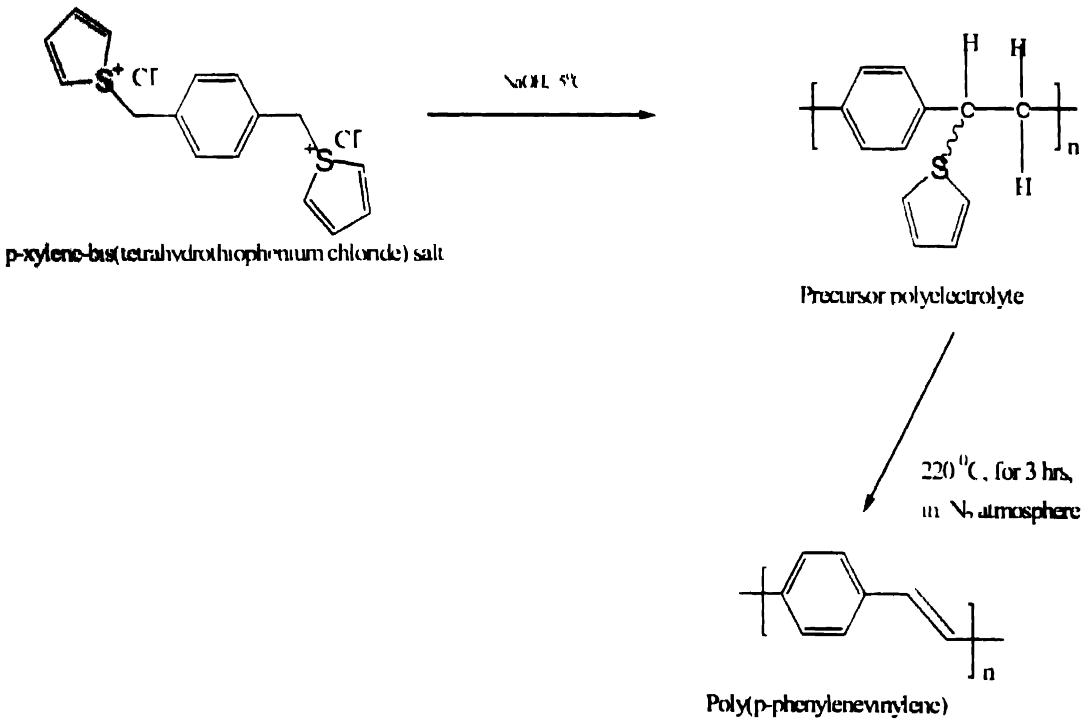
An important soluble precursor route for early PPV synthesis involved is the polymerisation of α,α'-dichloro-p-xylene by treatment with about one equivalent of potassium t-butoxide in non-hydroxylic solvents like tetrahydrofuran This methodology was first used by Gilch and Wheelwright and is referred to as Gilch route The reaction leads to a rather ill defined product with limited conjugation length and defects along the polymer backbone. Later, Wessling and co-workers developed one of the most important soluble precursor routes to PPV in 1960's The method was based upon aqueous solvent synthesis of poly(p-xylylene-α-dialkylsulfonium halides) from α,α'-bis(dialkyl sulfonium salts), followed by thermolytic formation of the final conjugated polymer The charged sulfonium groups solubilise the polymer and are removed during the conversion step. Molecular weights for the polyelectrolyte are in the 10,000 to 1,000,000 ranges, which may be precipitated or dialyzed to give typical yields of about 20% high molecular fraction.

Procedure of Synthesis

p-xylenebis(tetrahydrothiophenium chloride) salt (Aldrich) (21.8 gram, 0 6 mole) was dissolved in 150 ml of deionised water, by stirring, in a 3 neck flat bottom jacketed flask (500 ml) fitted with a teflon stirrer, resulted in a 0 4 molar solution The solution was cooled to –5 ^{0}C by passing cold mixture of methanol and water through the jacket and thoroughly purged with high purity dry nitrogen gas to remove any trace of dissolved oxygen present in it. In a separate beaker (250 ml), a solution of NaOH (0 4 molar strength) was prepared by dissolving 2.4 grams of NaOH in 150 ml of deionised water.

The base solution was also cooled to –5 ^{0}C and then transferred to a 250 ml additional funnel that was stoppered with a septum, fitted to the side neck of the 3-neck flask. This solution was also purged with nitrogen gas for 15 minute. An oil bubbler was fitted to the third neck as nitrogen outlet.

Once the solution has been cooled and purged the base solution was added to the monomer solution as quickly as possible with vigorous stirring. The reaction was completely carried out in nitrogen atmosphere. This mixture gave final reagent concentration of 0.2M. The viscosity of the solution increased rapidly over the first ten minutes and stirring become more difficult. The formation of precursor polyelectrolyte was allowed to proceed for 40 minutes. The indication of the successful reaction was the ability of the solution to visibly fluoresce under UV illumination.


Cl⁻
Cl⁻
S⁺
S⁺
p-xylene-bis(tetrahydrothiophenium chloride) salt
NaOH, 5 °C
H
H
C
C
S
H
n
Precursor polyelectrolyte
220 ^{0}C, for 3 hrs,
in N_2 atmosphere
n
Poly(p-phenylenevinylene)

Scheme: 3.1. Schematic of the synthesis of Poly(p-phenylene vinylene) by Wessling s route

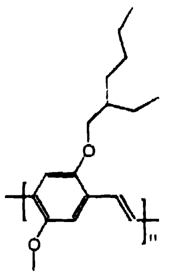
The reaction was then stopped and the unreacted base was neutralised with a dilute solution of HCl (6.5 pH) The neutralisation was done very slowly (over 40-60 minutes). Final purification of the aqueous precursor polyelectrolyte was accompanied by dialyzing against distilled water for 3 days using Sigma Dialysis cellulose membrane tubing with a reported molecular weight cut off 12,000 Daltons Dialysis removed low molecular weight impurities including residual reactants, the elimination products from the reaction and neutralization product, NaCl The end point of the dialysis was determined by the reversal in osmotic pressure (i e when the volume of the precursor polymer inside the dialysis bag began to increase) The yield of the precursor polyelectrolyte was about 22-25%

Precautions

1. The monomer salt should be dry and should be weighed under dry conditions.
2. The stirring should be maintained adequately
3. The oxygen has to be completely removed from the solution before mixing

3.1.b. Synthesis of poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylenevinylene]

A red colour polymer, derivative of PPV, Poly[1-methoxy-4-(2'-ethylhexyloxy)-p-phenylenevinylene] (MEH-PPV), is the extensively studied orange light emitting electroluminescent polymer. It is soluble in wide range of organic solvents, that makes the polymer easily processible and device can be fabricated more comfortably



The structure of MEH-PPV

Wudl et al first synthesized it via Gilch route The presence of a branched alkyl substituent, namely, 2-ethylhexyloxy group, and a dissimilar substituent, the methoxy group, at 4 and 1-position respectively on the aromatic ring, are key factors that impart high solubility to MEH-PPV The inability to pack effectively makes MEH-PPV readily soluble in a variety of organic solvents at the same time also reduces the level of inter-chain excitonic species, thereby leading to higher emission efficiencies

Procedure of Synthesis

Step 1. Preparation of 1-bromo-2-ethylhexane

A mixture of 2-ethylhexanol (S D Fine Chem Ltd) (130 g, 1 mole, 1 eq.) and red phosphorus (Yodoga Pharmaceuticls Co Ltd. Japan) (15 485 g, 0.5 mole, 0 5 eq.) was heated to 150 - 160 ^{0}C With the heating on, bromine (GSK Pharmaceuticals Ltd) (39 ml, 0.75 mole, 0 75 eq.) was added slowly drop wise in such a manner that the exothermicity of the reaction was under control. Heating was continued for 6 hours, the mixture brought to room temperature and diluted with water It was filtered under suction to remove excess phosphorus and phosphorous acid. The residue was thoroughly washed with ether (400 ml) and the filtrate was washed with water until neutral, then with a 10 wt % solution of sodium thiosulphate to remove excess bromine. It was dried over anhydrous

sodium sulphate, ether was removed by boiling off and the product was obtained as a colourless liquid after distillation at 76 ^{0}C at a reduced pressure (16 mm of Hg). It was stored in dark over anhydrous K_2CO_3 Yield. 146 gram (75%).

Step 2. Preparation of 1-methoxy-4-(2'-ethylhexyloxy)benzene

NaOH (16.7 g, 417 mmol, 1 0 eq.) was dissolved in ethanol in a 2-necked round bottom flask (500 ml) fitted with a reflux condenser and a nitrogen purger. Dry nitrogen gas was then bubbled through the solution for 30 minutes and the solution was warmed to 60 ^{0}C. With nitrogen purging, 4-methoxyphenol (Loba Chemie) (45 g, 363 mmol, 0.87 eq.) was added and it was allowed to reflux for 10 minutes. Then, the nitrogen gas flow was stopped and ethylhexyl bromide (prepared in step 1) (66 6 g, 345 mmol, 0.83 eq.), after being purged with nitrogen gas for 10 minutes, was taken in a dropping funnel and slowly added drop wise to the refluxing sodium methoxy phenoxide solution After the addition was complete, the solution was allowed to reflux for 24 hours, cooled to room temperature and ethanol was removed by using a rotary evaporator. Ether and water were added to it and the ethereal layer separated It was washed with 5% NaOH solution to remove any unreacted methoxy phenol and washed with water until neutral Ether was evaporated and, the product was collected as a colourless liquid by fractionally distilling at 140 ^{0}C at a reduced pressure of 0 1 mm of Hg Yield: 54 gram (65%)

Step 3. Preparartion of a,a'-dichloro-2-methoxy-5-(2'-ethylhexyloxy)xylene

A mixture of 1-methoxy-4-(2'-ethylhexyloxy)benzene (prepared in step 2) (15 g, 66.4 mmol, 1 eq.), 70 ml of dioxane, 45 ml formaldehyde (39%) and 65 ml concentrated HCl (35%) was taken in a two-necked round-bottom flask and the contents were saturated with HCl gas for 20 min. at 0 ^{0}C and stirred for 3 hours at room temperature.

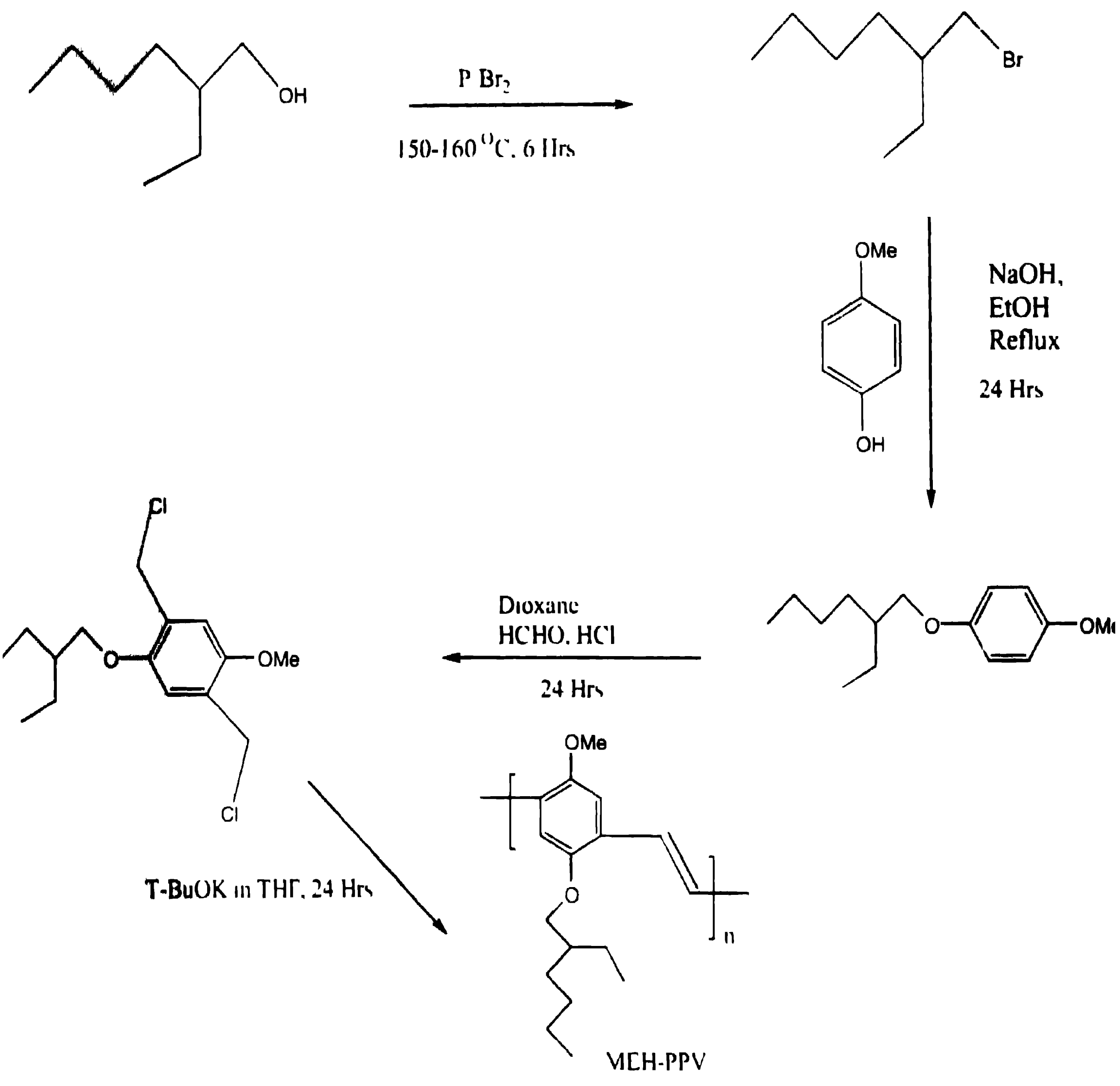
Treating ammonium chloride with concentrated sulphuric acid produced the required dry HCl gas. The outgoing HCl vapours were neutralized over an aqueous NaOH solution. Two additional batches of 25 ml formaldehyde were added followed by HCl gas purge for 3 hours. After addition was completed, the HCl purge was continued for 24 hours. [Caution: This reaction is known to generate chloromethyl methyl ether, a potent carcinogen]. The reaction mixture was cooled to room temperature and later in an ice bath when a pale greenish white solid precipitated out. It was filtered under suction, washed thoroughly with water until the washings were neutral, and then with ice-cold methanol. It was dried over anhydrous $CaCl_2$ in a vacuum desiccators at reduced pressure and purified by dissolving in hot petroleum ether (40-50 °C fraction) and precipitated from ice-cold methanol a white solid product, which was filtered, washed with cold methanol and dried at reduced pressure. Yield. 16 gram (72%) m.p: 58-60 °C .

Step 4. Preparation of Final Product (MEH-PPV)

α,α'-dichloro-2-methoxy-5-(2'ethylhexyloxy)xylene (prepared in step 3) was polymerised directly to Poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylenevinylene], (MEH-PPV) as follows:

A solution of 1.0 grams (3 mmol) of α, α'-dichloro-2-methoxy-5-(2'-ethylhexyloxy)xylene (prepared in step 3) and 20 ml of anhydrous THF was prepared. To this solution a solution of 2.12 grams (18 mmol) of 95% potassium tert-butoxide in 80 ml of anhydrous THF was added drop wise at room temperature with stirring. The reaction mixture was stirred at ambient temperature for 24 hours At the end of this time the reaction mixture was poured into 500 ml of cold methanol with stirring. The resulting red

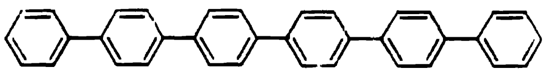
precipitate was washed with distilled water and reprecipitated from THF/methanol and dried under vacuum to afford 0.35 g (35% yield).



Scheme: 3.2. Schematic of the synthesis of MEH-PPV via Gilch route

3.1.[illegible] Synthesis of p-sexiphenyl

Aromatic hydrocarbons in the p-phenylenyl series have attracted considerable attention because of their good thermal stability, high melting points, insolubility and electronic configuration Previously, the individual, higher, isolable p-polyphenyls have usually been prepared by classical methods, such as the Ullmann coupling, Fittig coupling and the Grignard synthesis However these routes have one or more limitations.



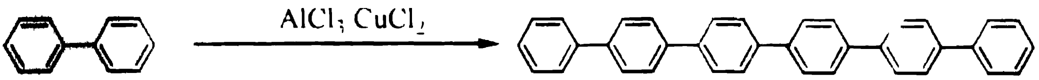
p-sexiphenyl

p-sexiphenyl, an oligomer , contains six benzene ring attached to each other at para position is thermally stable electroluminescent molecule This lower molecular weight oligomer like p-sexiphenyl can be prepared by the nuclear coupling of biphenyl in the presence of Lewis acid catalyst/oxidant system also known as Kovacic coupling.

Procedure of synthesis

Biphenyl (Merck) (77 gram, 0.5 mole) was taken in a three neck round bottom flask (2 litre) fitted with a teflon stirrer at the centre neck. The whole set up was emerged in a water bath to maintain a fix temperature of 80 ^{0}C throughout the reaction Reaction was carried out in nitrogen atmosphere throughout. When biphenyl melted completely anhydrous aluminium chloride flakes (Loba Chemie) (66.6 gram, 0.5 mole) was added in it and mixed by stirring thoroughly. Anhydrous cupric chloride (Loba Chemie) (33.6 gram, 0.25 mole), in small lots, was added slowly and addition was completed in ten minutes. The reaction was carried out for half an hours. The evolved gaseous

hydrochloric acid was titrated with NaOH solution. Then the molten mixture was quickly poured into 500 ml of 18% hydrochloric acid and steam distilled. After the residue was pulverized with water in a blender, it was treated with hydrochloric acid, triturated repeatedly with ethanol, and sucked dry. Trituration with concentrated hydrochloric acid was continued until the filtrate become colourless, followed by washing with boiling water until a negative test (silver nitrate) for chloride ions was obtained. The crude product, a light brown powder, was dried at 130 °C in vacuum oven. Yield 21.0 gram (28.8%).



Scheme: 3.3 Schematic of the synthesis of p-sexiphenyl via Kovacic route

The obtained product of p-sexiphenyl contained quadraphenyl as well as other higher molecular weight products. To obtain pure p-sexiphenyl fractional sublimation at 400 °C under high vacuum was carried out three times and sublimate was scratched from the glass tube. The melting point of the obtained product was found 453 °C, which is nearly equal to the reported value. Finally the product was dissolved in 1,2,4-trichlorobenzene and recrystallised. The obtained product was used for device fabrication.

3.2. Device Fabrications

3.2.a. Device fabrication using PPV as emitting layer

A double-layered light emitting diode with device structure ITO/PPV/CdS/Al was fabricated using PPV as emitting layer. The device was fabricated on a patterned indium tin oxide (ITO) (indium tin oxide is the mixture of In_2O_3 and SnO_2 in 91% and 9% respectively) coated glass substrate having a sheet resistance of 15 ohms/square. The substrate was cleaned in an ultrasonic bath using neutral Extran solution, distilled water, acetone and then with isopropyl alcohol. A film of precursor polyelectrolyte (Prepared in section 3.1 a) was spin coated on ITO coated substrate at a coating speed of 3000 rpm. The coated film was heated in nitrogen atmosphere at 220 ^{0}C for three hours to obtain about 20-50 nm thick PPV film. CdS was thermally deposited on the top of the films by vacuum evaporation technique. CdS layer, which is inherently n-type material, acts as an electron-transport layer in the device. A 200 nm thick layer of aluminium, as cathode, was then vacuum deposited onto the CdS/PPV layer using a shadow mask. Finally, the device was hermetically sealed under pure nitrogen in a glove box with 150μm thick glass slide using UV curable epoxy. The voltage was applied between these two electrodes using an Alpha Power Supply to get green emission under forward bias condition.

3.2.b. Device fabrication using MEH-PPV as emitting layer

A mono-layered light emitting diode with device structure ITO/MEH-PPV/Al was fabricated using MEH-PPV as emitting layer. A patterned indium tin oxide (ITO) coated glass substrate was cleaned according to the process carried out in section 3.2.a. An

amount (5mg) of polymer obtained in step 4 of the section 3.1 b was dissolved in 10 ml THF to obtain a solution of 0.5 mg/ml. MEH-PPV was spin coated on the substrate at a speed of 2000 rpm and it was dried under nitrogen atmosphere at a temperature of 70 ^{0}C. When all the residual solvent was removed a 200 nm thick layer of aluminium, as cathode, was thermally deposited under vacuum. Finally, the device was hermetically sealed under pure nitrogen in a glove box with 150µm thick glass slide using UV curable epoxy. The voltage was applied between these two electrodes using an Alpha Power Supply to get orange-red emission under forward bias condition

3.2.c. Device fabrication using p-sexiphenyl as emitting layer

A double-layered light emitting diode with device structure ITO/p-sexiphenyl/PBD/Al was fabricated using p-sexyphenyl as emitting layer A patterned indium tin oxide (ITO) coated glass substrate having a sheet resistance of 15 ohms/square was cleaned with Extran base solution followed by acetone and isopropyl alcohol, dried under vacuum and plasma treated Under a high vacuum of 10 [illegible] Torr a 50nm thick layer of polycrystalline p-sexiphenyl was vacuum deposited on this glass substrate as emitting layer followed by the deposition of 50 nm thick layer of 2,2-[1,2-phenylene-bis-(oxy)]bis(*N*,*N*-diphenylacetamide) (PBD) as electron transport layer And a 100 nm thick layer of aluminium was thermally vacuum deposited over that as cathode. Finally, the device was hermetically sealed under pure nitrogen in a glove box with 150µm thick glass slide using UV curable epoxy The voltage was applied between these two electrodes using an Alpha Power Supply to get blue emission under forward bias condition

Results and Discussion

Three organic materials, poly (p-phenylene vinylene) (PPV), Poly [2-Methoxy-5-(2'-Ethylhexyloxy)-p-phenylenevinylene] (MEH-PPV) and p-sexiphenyl were synthesized and light emitting diodes were fabricated using these materials as emitting layer. Materials and the devices were characterized by taking UV-Vis spectra, Furier Transform IR spectra, Thermo-grvimetric Analysis (TGA), Photoluminescence (PL) Spectra, Electroluminescence (EL) spectra and Current Voltage (I-V) Characteristics

Characterization of Materials and Devices

4.1.Characterization of PPV

4.1.a. UV-VIS Absorption Spectra of PPV and Precursor Polyelectrolyte

A film of PPV was prepared by spin coating of precursor polyelectrolyte obtained during the synthesis step of PPV on a clean fused silica substrate and thermally annealed at 220 ^{0}C for three hours in N_2 atmosphere UV-VIS absorption spectrum of the film was recorded on a Shimadzu UV-2401 spectrophotometer The absorption spectrum peaks of the film occur at 459 nm and 491 nm as shown in figure (4 1) The absorption spectra of the diluted solution of PPV precursor polyelectrolyte shows a prominent peak at 319 nm as shown in the figure (4 2) matches to the fluorescence seen under UV-light

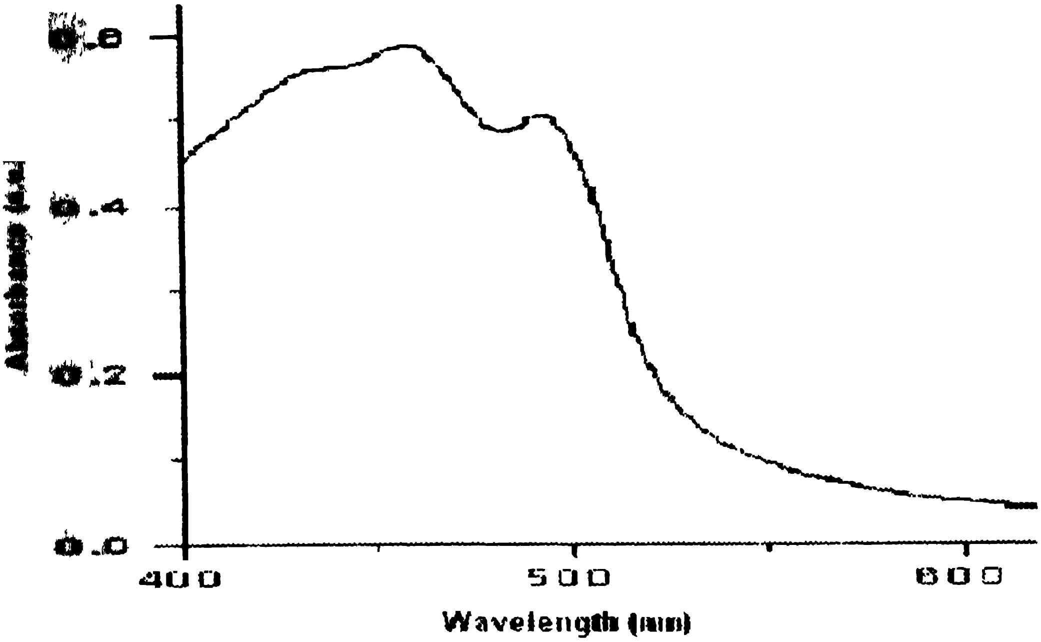


Figure: 4.1. UV-VIS absorption spectra of PPV film

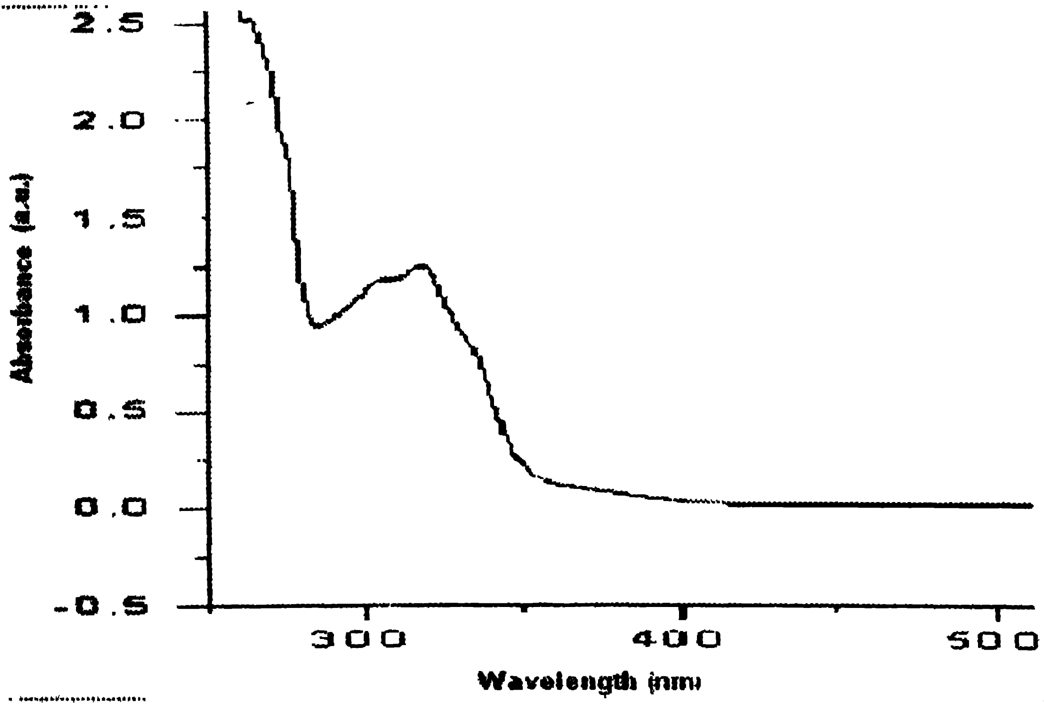


Figure: 4.2. UV-VIS absorption spectra of PPV precursor polyelectrolyte

4.1.3 Photoluminescence (PL) spectra of PPV film

Under UV illumination, PPV shows photoluminescence in the visible region The sample was illuminated with strong 360 nm radiations from a strong UV source Three characteristic peaks at 517nm, 551nm and 591 were observed as shown in figure (4 3). The peak at 551nm proves its green emission and other two peaks at 517nm and 591nm are due to the vibronic coupling

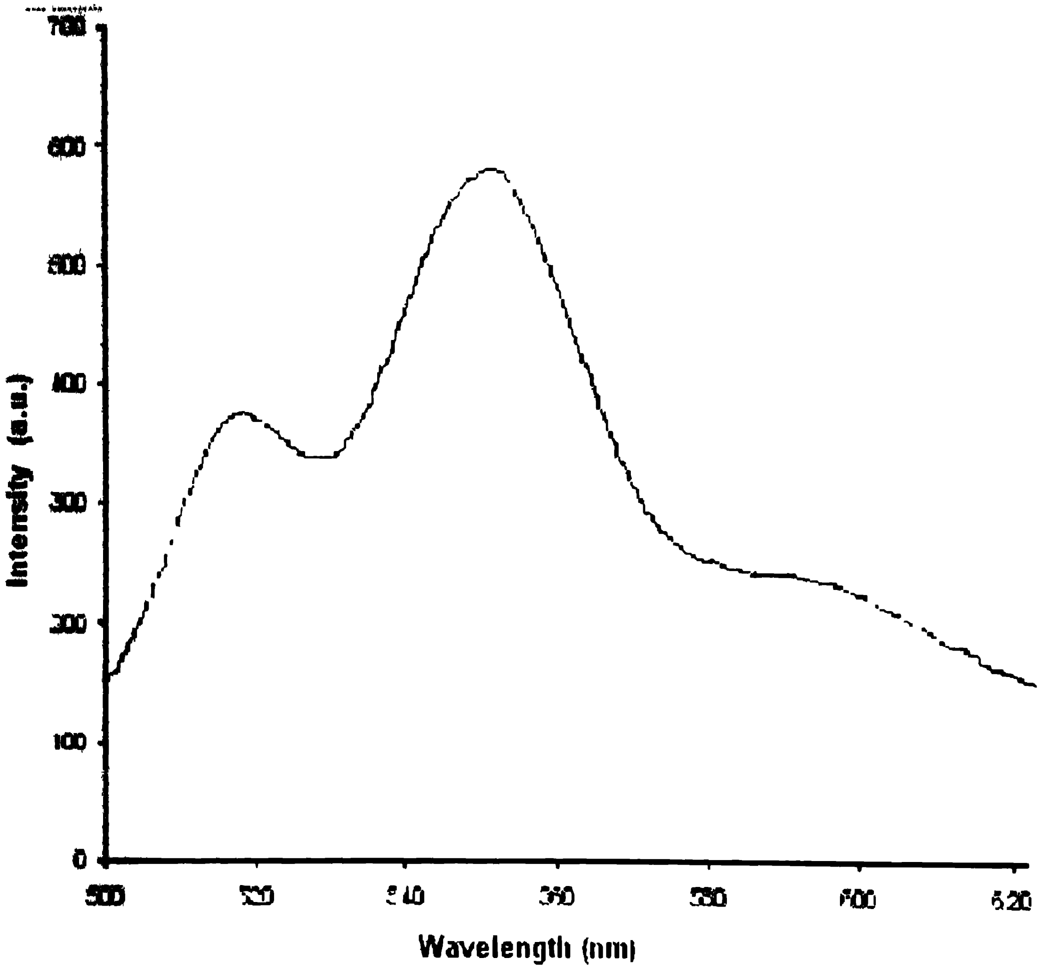


Figure: 4.3. Photoluminescence (PL) spectra of PPV film

4.1.c. Electroluminescence (EL) Spectra of PPV device

The electroluminescence (EL) spectrum of the ITO/PPV/CdS/Al device at different applied voltage is shown in figure (4 4) An increase in brightness was observed when voltage changed from lower to higher value On applying reverse bias no visible emission was observed from the device due to the blocking nature of the electrodes and the existence of a potential barrier at the junction between the PPV and CdS layers

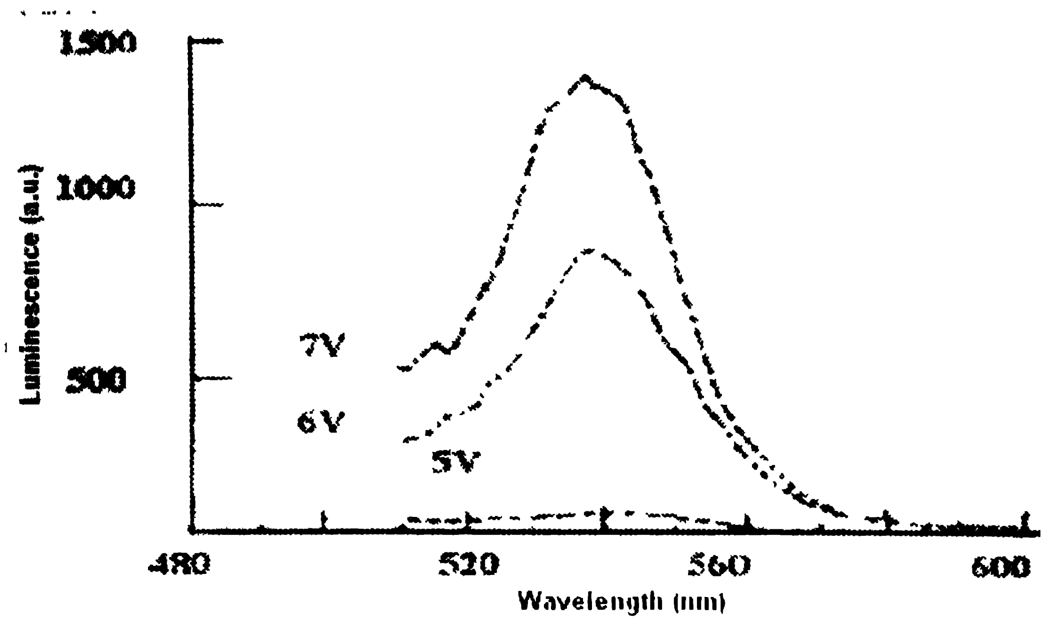


Figure: 4. 4. Electroluminescence (PL) spectra of ITO\PPV CdS\Al device

4.1.d. Current Voltage (I-V) characteristics of ITO\PPV\CdS\Al device

The current voltage (I-V) characteristics of the fabricated device were recorded by applying a dc voltage across the device with ITO as positive electrode and the aluminium as negative electrode (forward bias) The electroluminescence spectrum of the double-

layer device at different applied voltage is shown in the figure (4 5) The threshold of electroluminescence emission in this device is 5 V The greenish yellow light emission from the device was clearly visible under room light On increasing the voltage an exponential increase in the injection current was observed

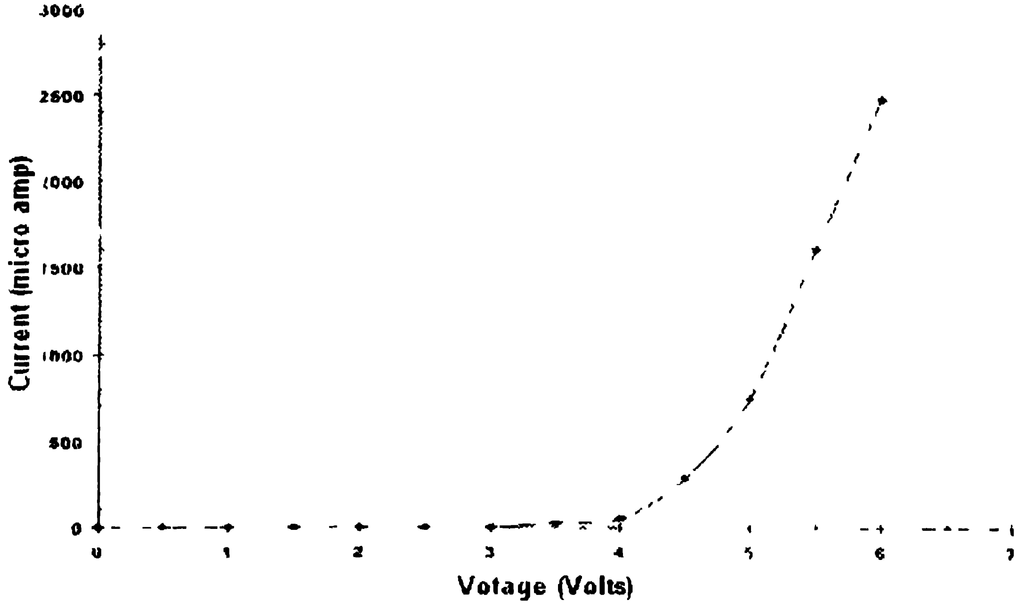


Figure 4 5 Current Voltage (I V) characteristics of ITO\PPV\CdS Al device

4.2. Characterization of MEH-PPV

4.2.a. UV-Vis Absorption Spectra of MEH-PPV

UV-Vis Spectra of the MEH-PPV film was recorded on a Shimadzu UV-2401 Spectrophotometer The sample was prepared by spin coating the solution of MEH-PPV in THF followed by drying at 70 ^{0}C in nitrogen atmosphere to remove residual solvent A

broad absorption peak was observed centred at 490 nm as shown in figure (4 6) is the characteristic peak of MEH-PPV

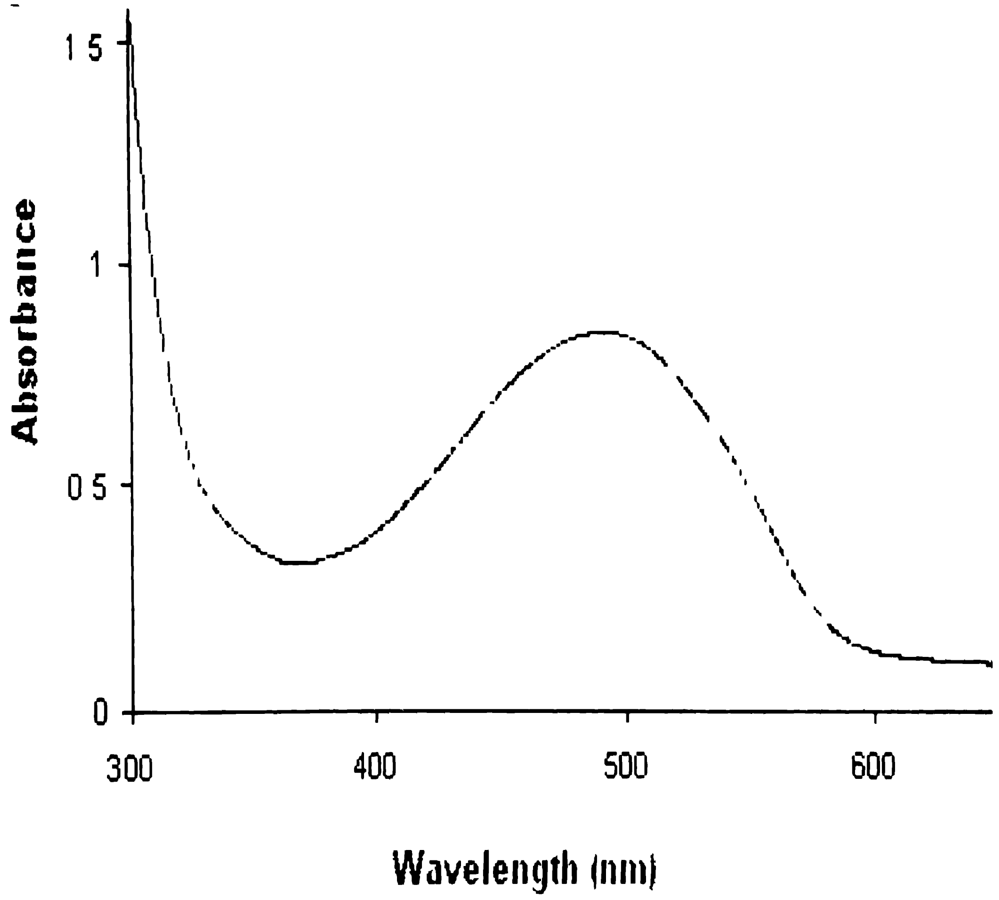


Figure 4 6 UV-VIS spectra of the MEH-PPV film on fused silica substrate

4.2.b. Themogravimetric analysis (TGA) of MEH-PPV

The Thermogravimetric Analysis (TGA) of the synthesized MEH-PPV was carried out on Mettler Toledo Star System and shown in figure (4 7) The TGA plot of the material shows a characteristic 27% loss in mass at 175 °C due to loss of substituents at 1,4-positions And a great mass loss is observed at 400 °C due to chain scissioning.

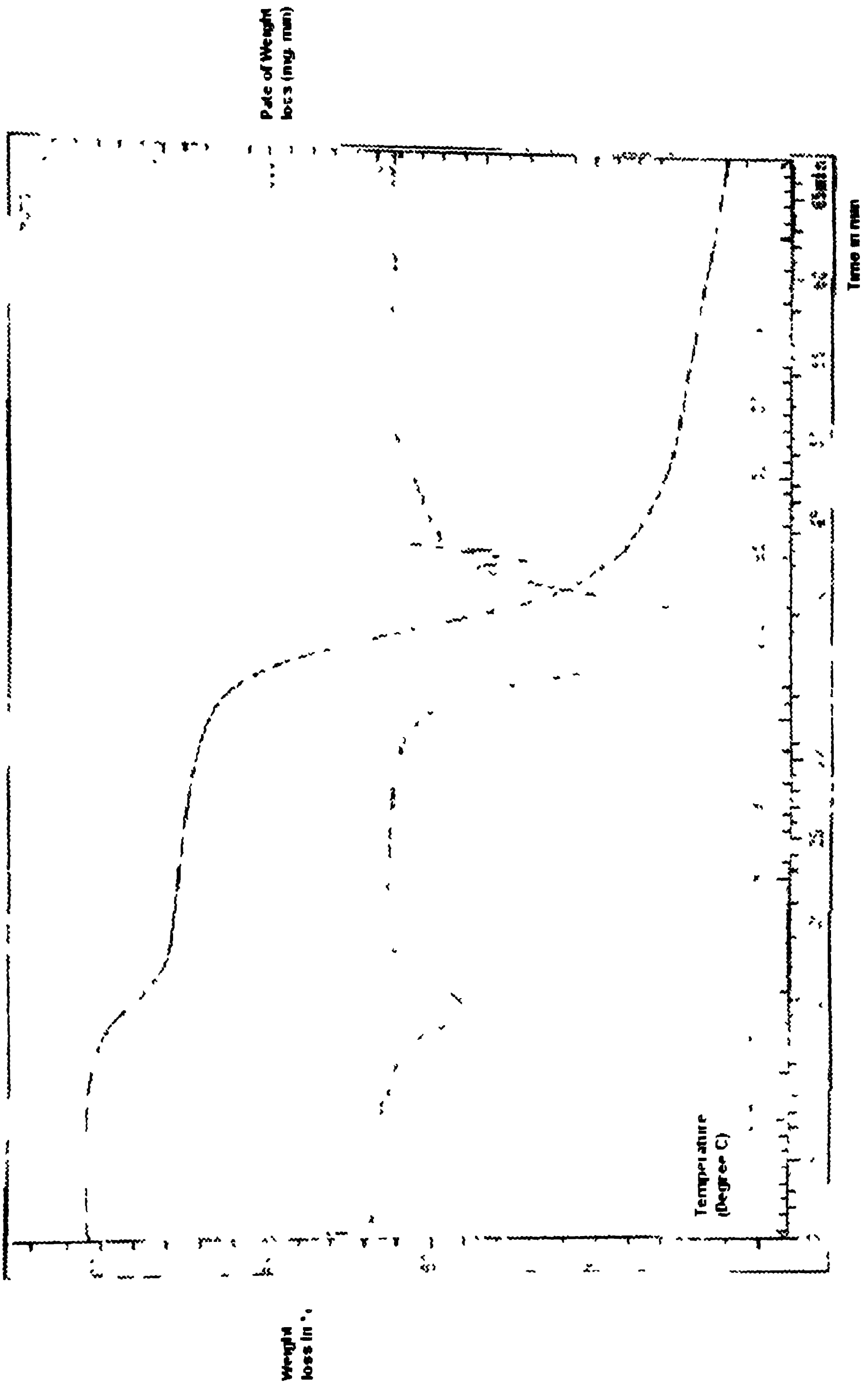


Figure 4.7 Themogravimetric analysis (TGA) of MEH-PPV

4.2.c. Photoluminescence (PL) spectra of MEH-PPV

Under UV illumination, MEH-PPV shows photoluminescence in the visible region The sample was illuminated with strong 360 nm radiations from a strong UV source Photoluminescence of MEH-PPV was carried out on film and in chloroform solution, only a characteristic peak was observed at 602 nm and 573 nm respectively with a shoulder at little higher wavelength as shown in figure (4 8 & 4 9) A blue shift is observed in solution with respect to film due to solvent effect The single peak is characteristics of orange- red emission and the shoulder is due to vibronic changes

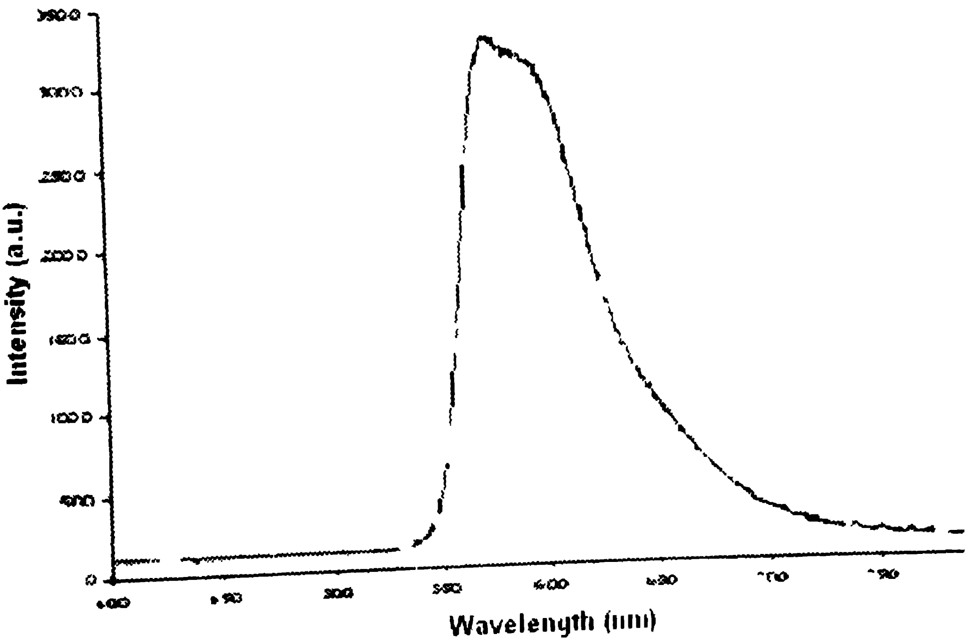


Figure 4 8 Photoluminescence (PL) spectra of MEH-PPV in Chloroform

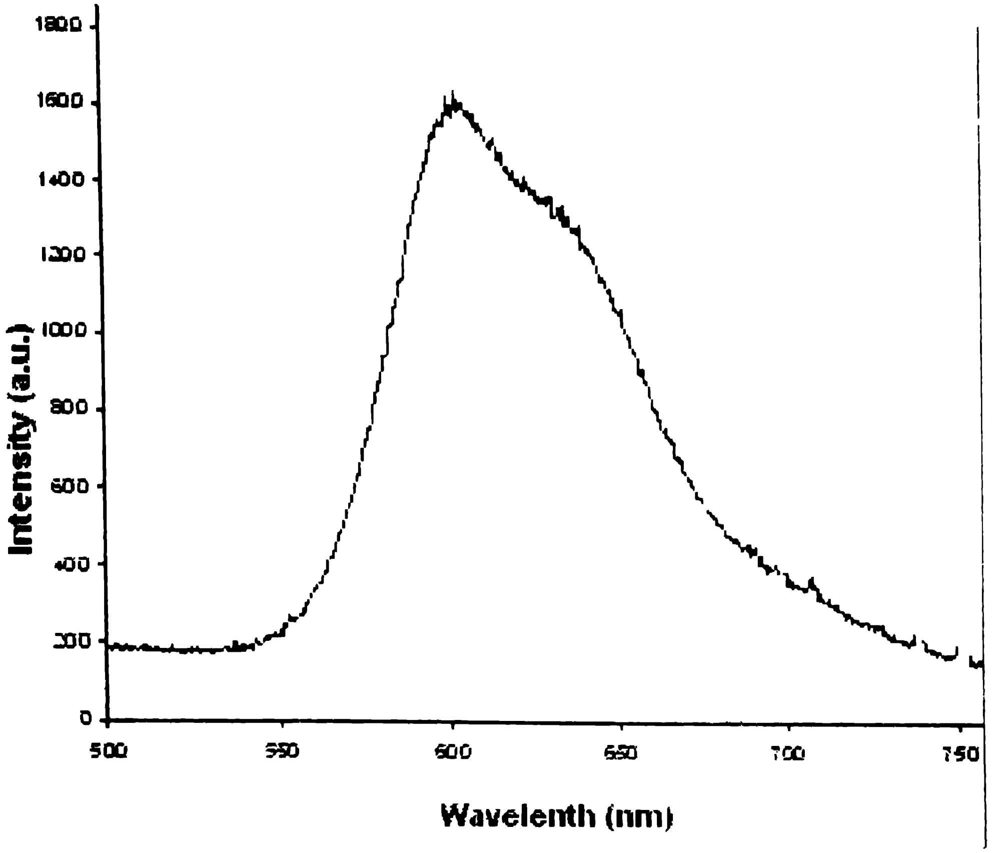


Figure 4.9 Photoluminescence (PL) spectra of MEH-PPV film

4.2.d. *Electroluminescence (EL) Spectra of MEH-PPV*

The electroluminescent (EL) spectrum of the single layer ITO\MEH-PPV\AL device was recorded applying a potential of 15 V across it. The photoluminescence maximum for MEH-PPV occurs at 602 nm, and the electroluminescence emission maximum is found blue shifted and occurs at 578 nm as shown in figure (4.10), and results in orange-red emission from the device. It was observed that the EL emission maximum was not dependent on the applied voltage and stayed fixed at 578 nm. Therefore the material could be used for orange red emitting device.

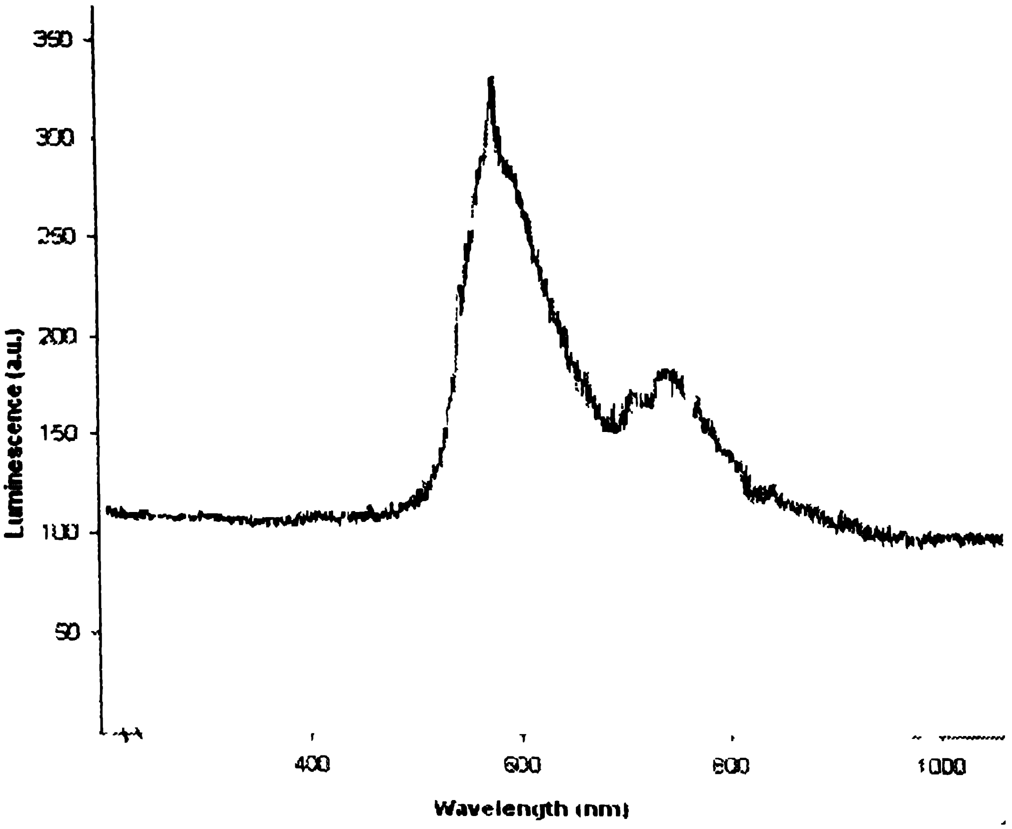


Figure 4 10 Electroluminescence Spectra of ITO\MEH-PPV\Al diode

4.3. Characterisation of p-sexiphenyl

4.3.a. UV-VIS Spectra of p-sexiphenyl

UV-Vis Spectra of the p-sexiphenyl was recorded on a Shimadzu UV-2401 Spectrophotometer The sample was prepared on fused silica substrates by thermal evaporation under vacuum The absorption spectrum peaks of the film found at 290nm and 318 nm respectively as shown in figure (4 11) All other peaks except one at 318 nm have not been resolved due to overlap of other bands, arising because of intermolecular interaction in the solid state

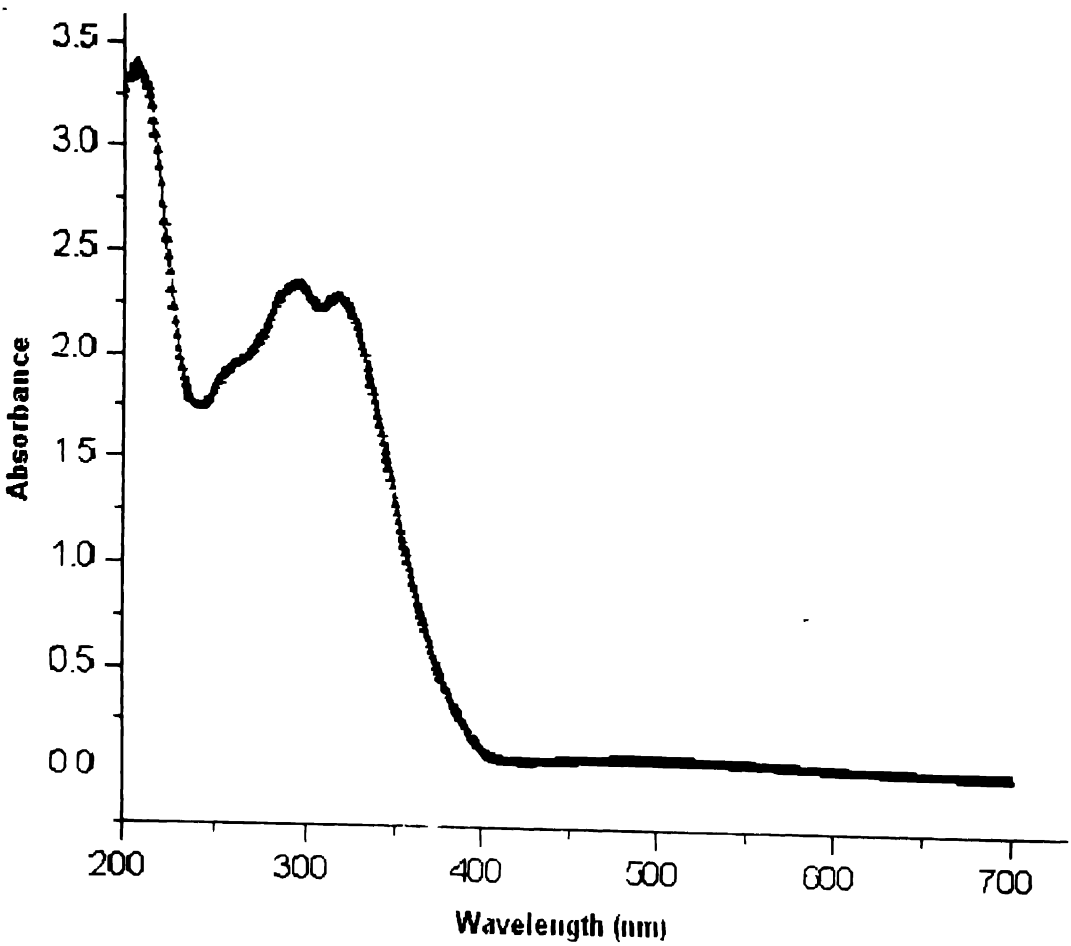


Figure 4.11 UV-Vis absorption spectra of p-sexiphenyl film on quartz substrate

4.3.b. Fourier Transform IR Spectra of p-sexiphenyl

A film of p-sexiphenyl was prepared on freshly cleaned KBr single crystal by thermal evaporation in vacuum and Fourier Transform IR spectra was recorded as shown in figure (4.12). The peak at 691cm^{-1} is due to out of plane deformation of ring. The peaks at 760cm^{-1} and 815cm^{-1} are due to out of plane vibrations of C-H on mono substituted and para substituted rings respectively. The C-C stretching in substituted rings is also seen at 1481.35cm^{-1}.

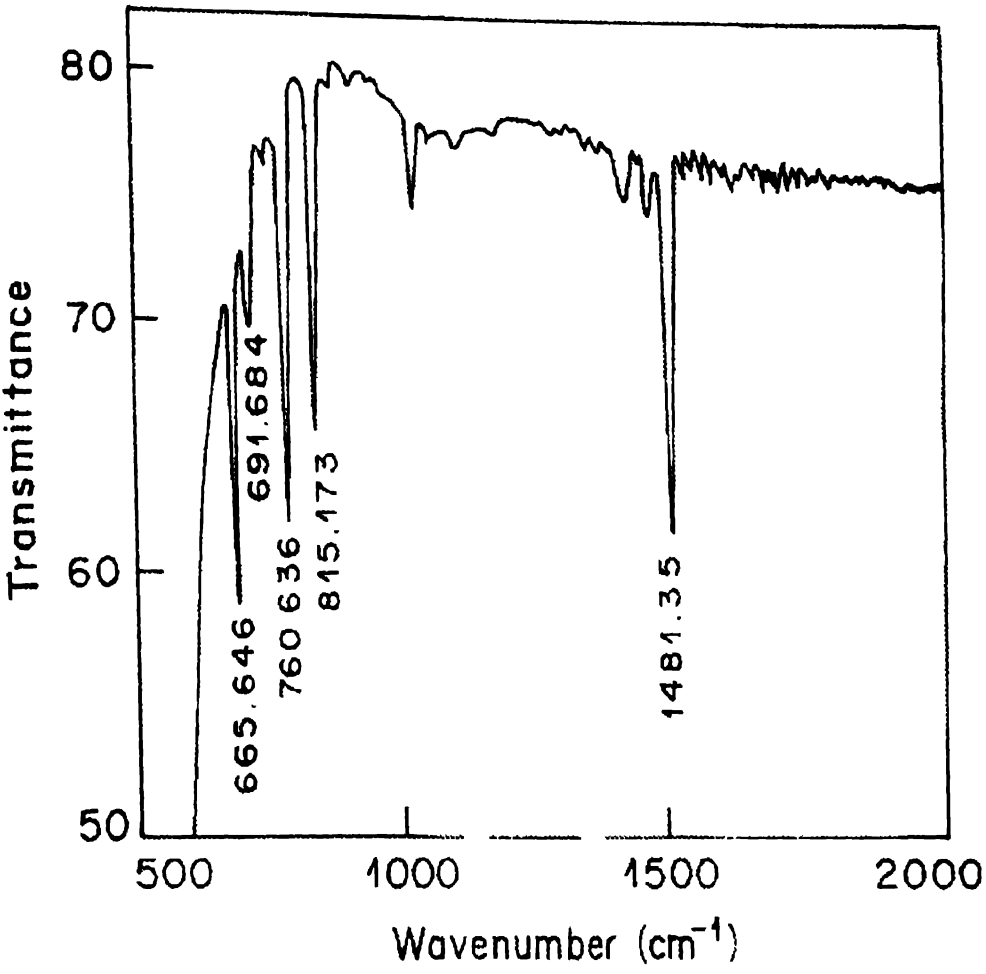


Figure 4 12 FTIR of p sexiphenyl on KBr single crystal

4.3.c. Photoluminescence (PL) Spectra of p-sexiphenyl

Under UV illumination, p-sexiphenyl shows photoluminescence in the visible region The sample was illuminated with strong 360 nm radiations from a strong UV source The PL spectrum shows the emission peaks at 423 nm and 485 nm respectively as shown in the figure (4 13) The peaks except at 423 nm arise because of the other oligomeric trace impurity and due to vibronic coupling in p-sexiphenyl

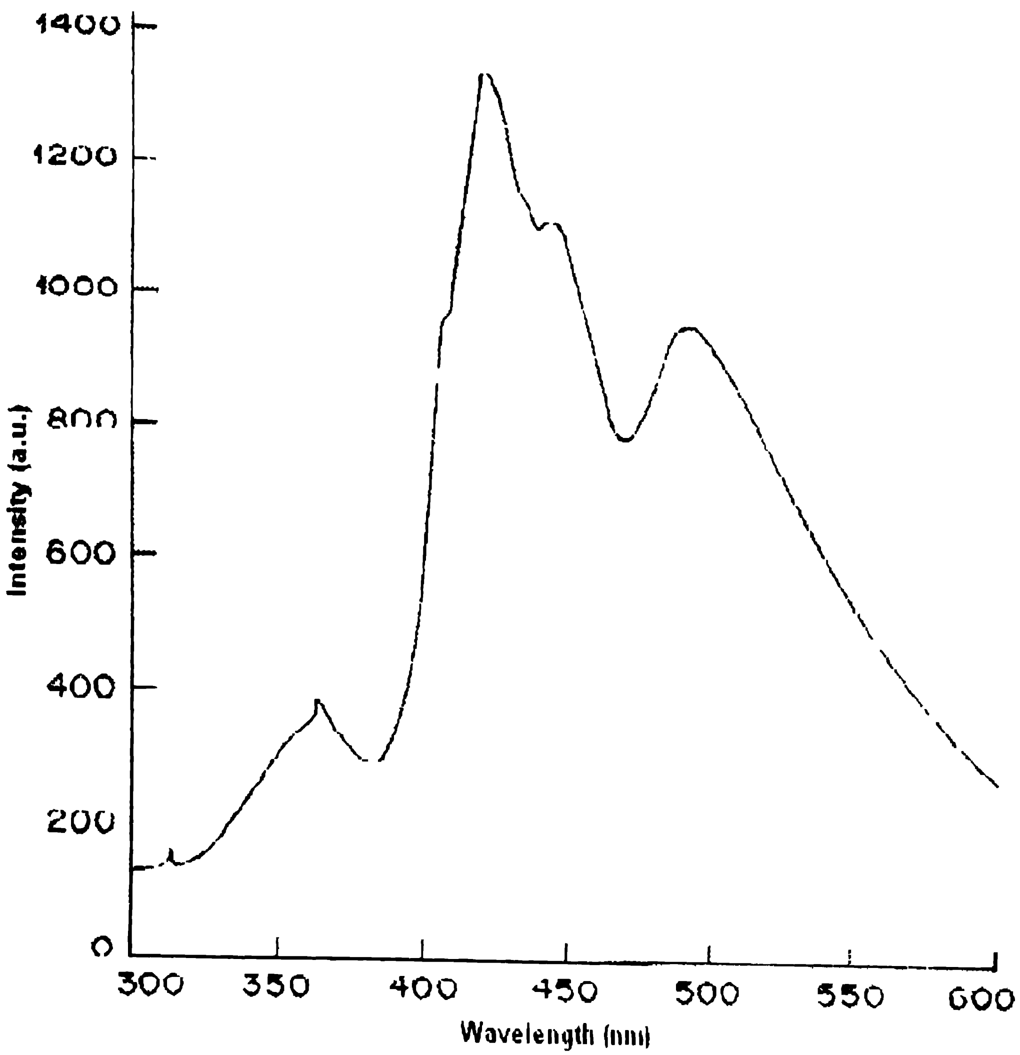


Figure 4 13 Photoluminescence spectra of p-sexiphenyl

4.3.d. Electroluminescence (EL) Spectra of p-sexiphenyl device

The electroluminescent (EL) spectrum of the double-layer device was recorded applying a potential of 12V across it Peaks at 400nm, 423nm and 450 are observed as shown in the figure (4 14) The peak at 423nm matches to the photoluminescence spectrum of p-sexiphenyl Two other peaks at 400nm and 450 are due to vibronic coupling.

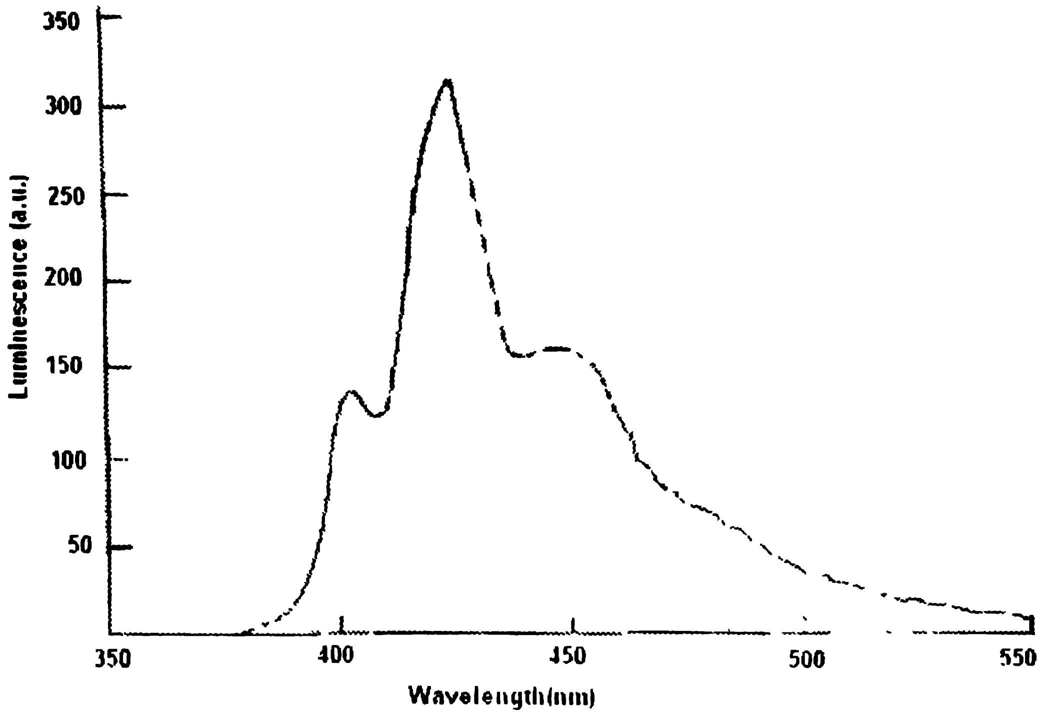


Figure 4 14 Electroluminescence spectra of p-sexiphenyl device

4.3.e. I-V Characteristics of p-sexiphenyl Device

The current voltage (I-V) characteristics of the fabricated device were recorded by applying a dc voltage across the device with ITO as positive electrode and the aluminium as negative electrode (forward bias) as shown in Figure (4 15) The current voltage (I-V) characteristics show that the current start rising above 6V indicates the onset of light emission (threshold voltage) The I-V characteristics of the device show highly non-linear nature with ohmic conduction at low voltage and trap limited conduction at high voltage. An intense blue emission was observed from the device on applying 12V potential across it.

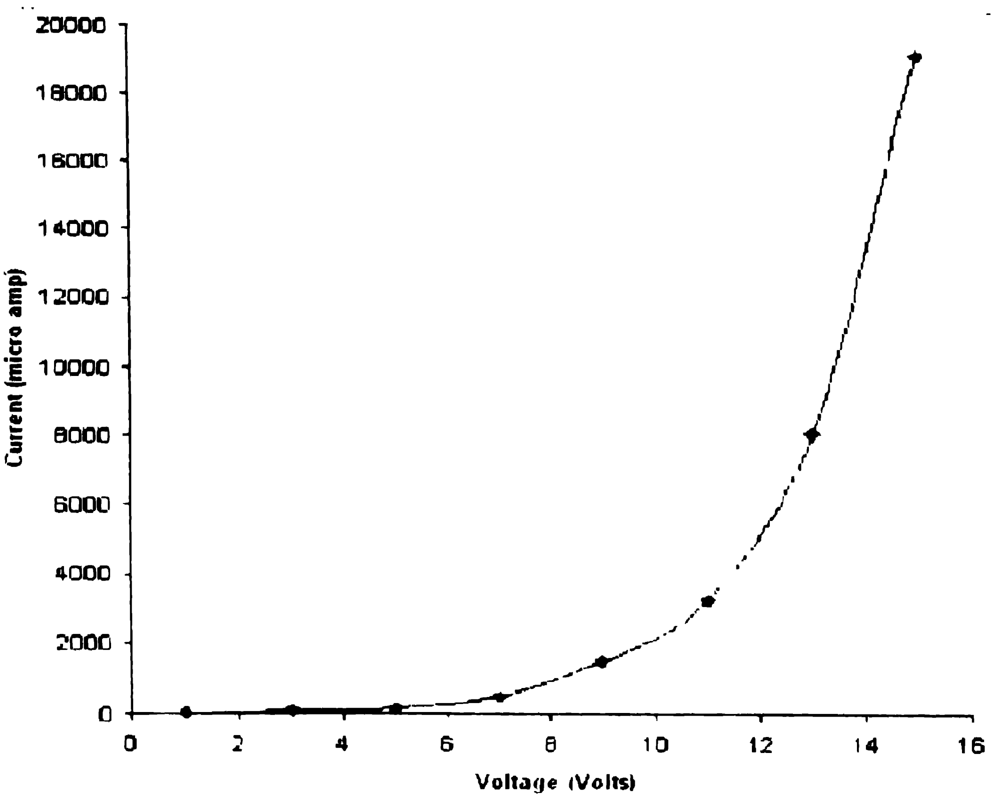


Figure 4.15. Current Voltage (I-V) Characteristics of p-sexiphenyl device

Conclusion

1. Poly(p-phenylenevinylene) or (PPV), poly[2-methoxy-5-(ethylhexyloxy)-p-phenylenevinylene] or (MEH-PPV) and p-sexiphenyl were synthesised by precursor polymerisation technique solution polymerisation technique and Kovacic method respectively And they were characterised by taking UV-Vis absorption spectra Fourier Transform IR spectra Photoluminescence (PL) spectra and Thermo-gravimetric Analysis (TGA)
2. The results of UV-Vis absorption spectra and Photoluminescence (PL) spectra of these material showed that the materials synthesised were of good purity
3. According to the Thermo-gravimetric Analysis (TGA) of MEH-PPV the thermal stability of the material is found up to 400 °C which is enough for OLEDs application
4. Three devices of the following configurations ITO/PPV/CdS/Al ITO/MEH-PPV/Al and ITO/p-sexiphenyl/PBD/Al were fabricated and their Electroluminescence (EL) spectra and Current Voltage (I-V) characteristics were measured
5. From the Electro luminescence (EL) spectra and Current Voltage (I-V) characteristics studies of the devices the following results were obtained
    - i The device with configuration ITO/MEH-PPV/Al required comparatively large bias voltage of nearly 15V for device functioning and produced an orange-red electro luminescence The large bias voltage required for device operation may be due to the mismatch in the energy level of electro luminescent material (MEH-PPV) and Al cathode
    - ii The devices with configurations ITO/PPV/CdS/Al and ITO/p-sexiphenyl/PBD/Al required a bias voltage of 5.6V for their operations and produced yellow-green and blue electro luminescence respectively The low voltage requirement may be due to the application of electron injection layer between the electro luminescent layer and Al cathode
6. The materials synthesised have shown a very good results in application of OLEDs therefore the synthesised materials have good prospects for industrial applications as electroluminescent materials in coming days

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Abstract

The Dynamic Source Routing protocol (DSR) is a simple and efficient routing protocol designed specifically for use in multi-hop wireless ad hoc networks of mobile nodes. DSR allows the network to be completely self-organizing and self-configuring, without the need for any existing network infrastructure or administration. The protocol is composed of the two main mechanisms of "*Route Discovery*" and "*Route Maintenance*", which work together to allow nodes to discover and maintain routes to arbitrary destinations in the ad hoc network. All aspects of the protocol operate entirely on demand, allowing the routing packet overhead of DSR to scale automatically to only that needed to react to changes in the routes currently in use. The protocol allows multiple routes to any destination and allows each sender to select and control the routes used in routing its packets, for example for use in load balancing or for increased robustness. Other advantages of the DSR protocol include easily guaranteed loop-free routing, support for use in networks containing unidirectional links, use of only soft state in routing, and very rapid recovery when routes in the network change. The DSR protocol is designed mainly for mobile ad hoc networks of up to about two hundred nodes, and is designed to work well with even very high rates of mobility. This document specifies the operation of the DSR protocol for routing unicast IPv4 packets.